LIGHT SCATTERING STUDIES

ON THE

POLYMERISATION AND SOLUBILIZATION

IN

DETERGENT SOLUTIONS.

By

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SUMMARY.

The thesis has been presented in two parts:-

Part I.

Many previous attempts have been made to measure the size of micelles in dilute detergent solutions by light scattering techniques. The principal difficulties encountered in this analysis are (1) the impossibility of measurement at concentrations below the critical micelle concentration (C.M.C. due to dissociation of the micelles, (2) the ionic nature of the micelles and (3) the possibility that the degree of aggregation of the micelles does not remain constant as the concentration is varied.

Instead of applying present theory, which involves some uncertainties, the suggestion was made that it may be possible to modify the micelles in such a way as to eliminate some of the difficulties and allow for a more concise analysis. This could be achieved by utilizing unsaturated soaps such as sodium oleate $CH_3(CH_2)_7CH{=}CH(CH_2)_7\ COO^-Na^+$, undecenyl trimethyl ammonium bromide (U.T.A.B.) $CH_2{=}CH(CH_2)_9N(CH_3)_3^+Br^-$

and sodium undecenyl sulphate (S.U.S.) $CH_2=CH(CH_2)_9OSO_3^-Na^+$. By causing polymerisation of the double bonds of the molecules in each separate micelle a 'polymicelle' may be obtained. A solution containing such 'polymicelles' would escape difficulties (1) and (3) while case (2) could be overcome for the carboxylic soaps by acidification after polymerisation and extraction of the polycarboxylic acid by organic solvents, in which light scattering measurements could also be performed.

The possibility that polymicelles, as envisaged above, could be formed with sodium oleate containing solubilized styrene is thwarted by the formation of a long chain polysoap, vastly different in size from the original micelle. The styrene oleate co-polymers (formed by irradiation with U.V. light and using azobisisobutyronitrile (A.B.I.N.) as initiator) have molecular weights dependent upon the styrene concentration.

The break in the Λ v's $\sqrt{C}$ curves (denoting the C.M.C.) is eliminated with solutions of S.U.S. after irradiation and

light scattering by the soap can be detected below the C.M.C. of the unirradiated soap. This indicates that there are few dissociable micelles left in solution. Measurements of $\left(\frac{dn}{dc}\right)_{\mu}$ electrolyte have been made and used in final analysis in preference to the $\left(\frac{dn}{dc}\right)_{c}$ electrolyte values employed by previous investigators in determining micellar weights in dilute salt solution. Evaluation of the refractive index increment at constant chemical potential of electrolyte involves dialysing soap solutions against respective salt solutions. This quantity cannot be determined for ordinary soaps as the micelles would simply dissociate and diffuse through the membrane.

The polymicellar weights obtained for S.U.S., both measured directly and by exprapolation of the solubilized styrene measurements, are in the region of 13,500. The value obtained by conventional means is 30,800. The discrepancy between the two values can be accounted for by incomplete polymerisation of the micelles and the possibility that there

is more than one polymerisation centre per micelle and termination is by disproportionation.

With U.T.A.B. the polymicellar weight (12,750) is close to the apparent micellar weight of 13,300. This indicates that most, if not all, the U.T.A.B. molecules within the micelles have polymerised together. There is a significant difference between the polymicellar weights (13,850 in 0.2M KBr) and micellar weights (19,700 in the same) in dilute salt solution. There is no measurable difference between the micelle weights of a saturated detergent and one containing an olefinic group so it can be argued that previous micellar weight determinations in dilute salt solutions are in error. The only way of correcting these micellar weights is by obtaining values for $\left(\frac{dn}{dc}\right)_{\mu}$ electrolyte, by using the dialysis method, which is only available for polymerised soaps.

Other well established features of micellar solutions are further corroborated. The C.M.C. decreases with added electrolyte and is lower for the higher homologue soaps.

Also the greatest dimension of the micelles remains below 200 A°.

Part II.

Information concerning the change in constitution of micelles accompanying solubilization was gathered by studying the light scattered by hexadecyl trimethyl ammonium bromide solutions containing some hydrocarbons and long chain alcohols.

The C.M.C. decreases monotonically with an increase in the concentration of solubilizate. This can be explained by considering the incorporation of a hydrocarbon as effectively increasing the chain length of the H.T.A.B. molecule.

Droplets of solubilizate formed below the C.M.C. causing a vast increase in the light scattered by solubilized systems. Above this concentration the micelles are of fixed composition.

The increase in micellar weight of a soap on solubilizatio is accounted for not only by the incorporation of hydrocarbon in the paraffin interior but also by an increase in the number of detergent molecules per micelle. With polar additives

the lowering of the association number on solubilization is attributed to replacement of some of the soap molecules by additive.

Difficulties are encountered with benzene as the solubilizate due to its appreciable water solubility. An estimate has been made of the benzene partition coefficient between micelles and water, though difficulties arise with the adoption of a suitable micellar model for these calculations.

The long chain alcohols octanol and decanol are not completely solubilized below the visible saturation limit for solubilization. This is thought to be due to their proximity to the aqueous layer.

FORM OF THESIS.

The thesis has been presented in two parts:-

Part I. Comprises some of the past work on detergent solutions and the difficulties encountered in the interpretation of the results from light scattering by these solutions, together with results obtained from an attempt to develop a new method of determining the sizes of micelles in detergent solutions, involving the polymerisation together of all the molecules in a micelle. The experimental results are discussed in the light of current knowledge in the field of detergent solutions.

Part II. Comprises the results and discussion of an investigation into the phenomenon of solubilization by means of the light scattered by detergent solutions containing organic additives.

PART I.

POLYMERISATION IN SOAP MICELLES

INTRODUCTION.

General : The properties of aqueous solutions of paraffin chain salts have been the subject of extensive study for many years. McBain (1) first noted their unusual behaviour from the observation that the conductivity of soaps was considerably greater than would be expected from their osmotic activity. He suggested that this could be explained in terms of the formation of colloidal aggregates, or ionic micelles, in solution. It is now generally accepted that above a certain concentration paraffin chain ions in solution are aggregated into micelles, though there is still much uncertainty in the detailed interpretation of the properties of these solutions. They have been found to exhibit interesting phenomena obeying general physical principles but are not, as yet, open to precise quantitative interpretation.

The special properties of ionic detergents are a result of the dualistic nature of their molecules, the paraffin chain being hydrophobic and the ionic end group hydrophilic. The ionic group makes the salts soluble in water

while the hydrophobic tail opposes molecular disperaion because of the large interfacial tension between paraffin and water ($\sim$ 59 ergs/$_{cm^2}$). The dipole-dipole forces between water molecules are much greater than the van der Waals-London forces between paraffin chains and the dipole-induced dipole forces between water and paraffin. The result is that on dissolving paraffin chain salts in water, clusters of paraffin chain ions are squeezed together by the surrounding water molecules, the ionic heads forming round the periphery of the micelle.

At extremely low concentrations the paraffin chain salts behave as strongelectrolytes. The micelle formation sets in at a rather definite concentration called the critical micelle concentration (C.M.C.) which is indicated by a distinct change in the solution properties such as surface tension, electrical conductivity, vapour pressure and specific volume. The C.M.C. is generally determined by the point of intersection of lines extrapolating some property of the system from below and from above the region of greatest change.

Micelle Structure:- The subject of micelle structure was being very actively developed about 25 years ago. At that time a number of models had been proposed, each having its staunch defenders. The current views on micelle architecture, shared by most of the leading investigators in this field, seems to be that several different micellar structures are possible and in fact exist. Which of these structures exists in any particular system depends entirely on the parameters of the system. These include the chemical nature of the colloidal electrolyte, the solvent, and any other components of the system such as salts, solubilized material, temperature and concentration of each component.

Among the different types of micelle which have been postulated the two most widely supported are the spherical and lamellar.

McBain (2) proposed the existence of ionic micelles consisting of about 3 or 4 molecules, along with neutral lamellar types. The basis for these postulates is to be found in the separation of soap into ionic and neutral micelles (due to the inclusion of the gegen ions) by ultrafiltration claimed by McBain and Jenkins (3), the

decrease in conductance observed beyond the C.M.C. and the shape of the diffusion coefficient v's concentration curve (4), which shows a pronounced minimum at the C.M.C.. It was found that when potassium laurate and sodium oleate solutions were ultrafiltered, through pores smaller than 75 mμ. dia., the filtrates had approximately constant concentration, irrespective of the initial concentration of the solution. It was claimed that the larger neutral micelles are unable to pass through the filter. However, the fact that only the smaller species can pass through is no proof at all of the existence of neutral micelles. If one makes the reasonable assumption that above the C.M.C. the monomeric ion concentration is approximately equal to the C.M.C.value, then the concentration of the filtrate should be that of the C.M.C. and should remain constant. As the single species are removed more of the micelles must dissociate to restore the micelle—monomeric ion equilibrium. The minimum in the diffusion coefficient curve can also be explained in terms of an ionized spherical micelle without recourse to a neutral micelle.

Stauff (5) has also inferred the presence of two types

of micelle, mainly from Xray diffraction studies. At moderate to high concentrations a long-spacing diffraction band appears, which Stauff has attributed to the presence of lamellar micelles. As the concentration of paraffin-chain salt is decreased, the spacing increases (interpreted as inclusion of water between the layers of paraffin-chain ions) and the intensity of the band decreases. By plotting the diffraction intensity against the concentration and extrapolating to zero intensity, Stauff concludes that the lamellar micelle exists only at high concentrations and that the colloidal effects observed at lower concentrations are due to a small spherical micelle. Dervichian (6,7) has suggested, however, that there is only one type of micelle and that the long spacing diffraction band is due to an intermicelle spacing which only appears after the concentration of micelles reaches a certain limiting value. Mattoon, Stearns, and Harkins (8),(9) agree with this and present as evidence a second long spacing band which they attribute to the single micelles.

A modification of McBains lamellar micelle was proposed by Philippoff (10). It is suspect however in that there is

considerable exposure of the paraffin portion of the micelle to the water. Even at high concentrations, in the anisotropic regions, this is very doubtful. One serious objection to the proposal of a lamellar micelle in dilute solution is that being microcrystalline it would be formed with a large negative entropy change. This is not in agreement with experimental data.

Hartley (11) believes that the properties of solutions of paraffin-chain salts are explainable with the assumption of only one type of micelle, if one takes into account the large interionic effects due to the electrical charge of the micelles. As experimental evidence of the existence of large interionic effects, he refers to measurements of electrical conductivity at high frequencies (12) and at high field strengths (13). Both of these investigations, while not conclusive, indicate the existence of large interionic effects. From his evidence Hartley concluded that the micelle is spherical with an essentially liquid-like arrangement of the paraffin chains in the interior protected by the ionic groups round the periphery. To support his theory he points out (14) that there is no

indication of hysteresis in the conductivity of a freshly diluted solution of a colloidal electrolyte, hence there can be no elaborate organisation in the micelle to effect a delay in formation.

Further indication of a non crystal like micelle rests in the fact that the C.M.C. is not specific for the nature of the gegenion and depends very little on the nature of the end group and that micelles form equally readily when salts with different end groups of like sign or different gegen ions are mixed. Diffusion (15,16,17,18) and ultracentrifuge (19) measurements indicate micellar radii which are in agreement with expectation from the spherical micelle. Thus, the direct experimental evidence as to the size of the micelles indicates, at least at concentrations just above the C.M.C., a micelle radius approximately equal to the length of the paraffin chain ion. A micelle of this size, having an interior density equal to that of a liquid paraffin would contain about 50 ions in the case of a twelve carbon chain and about 90 for a sixteen carbon chain.

McBain frequently expressed objection to the ionized spherical micelle of Hartley on the grounds that such a

micelle should have a conductivity $n^{2/3}$ greater than that of the single species, n being the number of single species in the micelle. Hence, McBain argued, the conductance of a colloidal electrolyte should increase, not decrease, above the C.M.C.. The rejection of the Hartley micelle on these grounds resulted from a misconception of what Hartley implied in his spherical micelle, namely a partially charged micelle in which gegenion reduced the total charge of the micelle from n units to some smaller value x. Van Rysselberghe (20) showed that such a micelle would have a molar conductance $\lambda x^2/n^{1/3}$. The conductance of a given solution containing micelles with charge x and size n would therefore be $x^2/n^{1/3}$ times that of the same solution containing the solute as single ions. This ratio will certainly be greater than unity if $x = n$, but if $x \approx 0.2n$ the ratio is of the order of unity for $n \approx 100$ and can assume very small values for $x < 0.1n$ even when $n \approx 100$.

Debye and Anacker (21) and later Trap and Hermans (22), on the basis of light scattering data obtained with C_{14} and C_{18} quaternary ammonium compounds in the presence of salt,

produced evidence for a rod-shaped micelle with a length of several hundred Angstroms. In this model the ions are arranged about a cylindrical axis with tails pointing inward and heads pointing outward. This micelle, which can be formed by lateral distension of a Hartley micelle, fits well with theoretical calculations on energy of formation. However their measurements were made close to the salting out region of their detergent and there is a possibility that they were determining the particle weight of crystallites of detergent rather than micelles.

Recent papers by Tartar and co-workers (23) pursuing the theory of Klevens (24) and Harkins (25) report studies on micellar molecular weights of 21 detergents with chain length of 8 to 16 carbon atoms. Sulphate, sulphonate and ammonium types were studied by light scattering, electrical conductance and diffusion techniques. The micelle shapes were found to vary from spherical to oblate spheroid, depending on the chain length and area occupied per polar group on the surface. One dimension - the semiaxis - does not exceed the maximum stretched - out length of the hydrocarbon chains. The interior of the micelles was in a 'liquid' state of disorder

except for the spacing arrangement of the chain due to the polar end groups.

The evidence for the inclusion of gegen ions in the micelle is considerable. Aggregation of ions all of one sign would lead to an increase in conductance (1), whereas the equivalent conductance is usually observed to fall above the C.M.C.. The transport number of the gegen ion is sometimes negative (26) owing to the transference of attached gegen ions by the micelle in the opposite direction from their motion when free. The yellow colour of aqueous solutions of cetyl pyridinium iodide (27) is attributed to a firm attachment between the ions. Light scattering measurements can give an idea of the order of magnitude of the residual micellar charge.

The evidence concerning the arrangement of the paraffin-chains in the micelle is so far inconclusive. Hartley (11) has argued for a random arrangement similar to liquid paraffin, both on the basis of probability and from a consideration of the lack of specificity in the solubilization of water-insoluble organic molecules by aqueous solutions of paraffin chain salts. Similarly Corrin (28) has found that

the relationship between the amount of oil dissolved and the increase in Xray spacing is in somewhat better agreement with a spherical micelle i.e. random internal grouping than the cylindrical model. The fact that the Xray spacing increases however only indicates that there is an enlargement of the micelles on solubilization. No direct evidence can be formed from these measurements to support any single micelle shape.

We can conclude from the above considerations that the existence of Hartley micelles, consisting of rather small spherical or ellipsoidal clusters of monomers, in dilute detergent solutions, is fairly well established. It is probable that at higher concentrations, or under the influence of added electrolyte, different types of micelle exist, depending on conditions and that transitions from one type to another type can occur.

Micelle Size Distribution:- Several arguments have been advanced to support the assumption that all micelles in a soap solutions have approximately the same size and that this size does not depend much on concentration.

In 1949 Debye (29) outlined a general theory of micelle

formation. This theory was intended to explain why micelles do not grow indefinitely and separate out as an ordinary phase. Debye assumed that the micelles were disc shaped and that as the micelle grows each entering detergent ion releases the same amount of hydrocarbon-chain adhesional energy, so that this energy is proportional to the size of the micelle. He derived that the total work of assembling, the micelle is

$$W = N^{\frac{3}{2}} We - NWm \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where N is the number of detergent ions in the micelle, Wm is the work of hydrocarbon-chain adhesion and We is a constant which relates to work done against electrostatic repulsion of the ionic head groups. Plotting W against N gives a curve with a minimum. Debye considered the value of N at which the minimum occurs to specify the stable micelle size since 'work is required to increase or decrease the equilibrium number No'.

In deriving equation 1, the effect of gegenions in screening the electrostatic repulsion between head groups is neglected. Hobbs (30) attempted to refine the theory by

taking into account the effect of the gegenion atmosphere, but mathematical difficulties prevented the development of general equations. Reich (31) and Hemans (32) have raised several objections to the above theory. Firstly the stable micelle size (or size distribution) must be that which results in minimum free energy for the system. This is quite different from the criterion of minimum free energy per micelle. Also growth of micelles will involve a decrease in the number of independent particles in the system and hence will involve a decrease in total entropy. This is omitted in Debye's treatment. Lastly the energy of hydrocarbon chain adhesion per ion must increase as the micelle grows. If it remained constant as Debye assumes, growth beyond dimer size would not occur. His assumption that W_m is constant appeared to lead to a preferred micelle size only because of the incorrect minimization of energy per micelle instead of energy of the system.

Of late micelles have been treated theoretically as a product of the reaction of single molecules to form clusters with an associated equilibrium constant (31,33). Shinoda and others (34,38) have considered micelles to be a different

phase and the thermodynamics of phase equilibria is invoked. Hoeve and Benson (39) and Aranow (40) have studied the statistical mechanics of micellar systems using Hill's theory (41) of physical clusters and the ensemble natural for constant temperature, pressure and quantity of solvent. Shinoda's energy calculations for the micelle 'phase' are related to the energy change involved in adding or removing a molecule from the most probable micelle. Aranow points out that this relationship displays the reason for the sucess in some calculations of theories which postulate only a single micelle size; only the most probable micelle need be considered in any calculation involving chemical potential. Statistically the development of a cluster theory for ionic detergents is attended by certain difficulties which are part of the general problem of electrolyte theory. There is for instance the necessity of assuring weak interaction among the members of the statistical ensemble while allowing the number of molecules of a charged species to vary from zero to infinity. Clearly, the condition exists that some members of the ensemble will have infinite charge and in this case will

interact strongly with other members of the ensemble.

In spite of the difficulty in deriving theoretically a narrow micelle distribution there is some experimental evidence in favour of monodispersity:—

(a) the electrical conductivity can be explained on the assumption of a single micellar size (42)

(b) the effect of concentration on light scattering is very similar to that observed in solutions of macro - molecules where the solute has a molecular weight independent of the concentration. The interpretation of the light scattered by detergent solutions is, however, complicated by charge effects which makes it difficult to conclude anything definite about the micelle distribution from the light scattering data.

(c) Phillips (43) has found constant values for the ionic product $[Na^+] \times [monomer^-]$ in solutions of an anionic soap. Since his calculation is based on the assumption that only one micellar weight occurs, it is tempting to conclude conversely, that his results confirm this assumption.

Light Scattering Theory:- When a beam of light passes through a medium it sets up oscillating electric moments in the particles composing it. These act as secondary sources of radiation which has the same wavelength as the incident radiation, thus producing scattered light. Some of the absorbed radiation is used to raise the molecules to higher energy states. This is re-emitted as Raman lines of different wavelength. The intensity of this radiation is usually several orders of magnitude smaller than that of the scattered light and may be neglected.

The calculation of the scattering by a system may be approached in two ways. The first is by treating the scatter as the result of statistical fluctuations of density and concentration causing fluctuation in the optical dielectric constant. This Fluctuation Theory of light-scatteringwas developed by Einstein (44), Smoluchowski (45) and others and is found most useful for systems of interacting particles, as in liquids and concentrated solutions. The other method is by calculation of the scatter from each independent particle followed by summation over all the particles, taking into account the interferences producing phase

differences. This is termed the Interference Theory and was developed by Rayleigh (46), while Zimm (47) showed its application to dilute non-interacting solutions of high polymers. The principal assumption in the Interference Theory is that the scattering particles are sufficiently far from each other for their relative positions to be random. The existence of a high degree of order in liquids has been demonstrated and the loss in intensity due to destructive interference can be considerable (about 50%). Thus the Fluctuation Theory will be considered in detail along with relevent sections of Rayleigh's treatment.

When the particles comprising an ideal gas are subjected to an electric field such as that associated with a light wave having a field strength of E, a dipole is set up in the particle the magnitude of which is proportional to E.i.e.

$$p = \alpha E \qquad \ldots\ldots\ldots\

where x is the particle co-ordinate in the direction of propagation, λ is the wavelength of the light, t the time, ν the frequency and Eo the amplitude. The field is periodic and an oscillating dipole is produced.

$$p = \alpha E_o \cos 2\pi \left(\nu t - \frac{x}{\lambda} \right) \qquad (4)$$

Such an oscillating dipole is a source of radiation the amplitude of which Es is proportional to $\frac{d^2p}{dt^2}$. If we consider a distance r from this dipole which is large compared to the wavelength of the light, the value of Es will also be proportional to sin ϕ_1 where ϕ_1 is the angle between the axis of the dipole and the line from the particle to the point at distance r. Also Es will vary inversely as r, provided r is very much greater than λ.

$$E_s \propto \frac{d^2p}{dt^2} \cdot \frac{\sin \phi_1}{r}$$

It can be shown that the proportionality constant in this equation is $\frac{1}{\bar{c}^2}$; $\bar{c}$ is the velocity of light so that

$$E_s = \frac{4\pi^2 \nu^2 \alpha E_o \sin \phi_1}{\bar{c}^2 r} \cdot \cos 2\pi \left(\nu t - \frac{x}{\lambda} \right) \qquad (5)$$

The quantity measured experimentally is the intensity, which is proportional to the square of the amplitude or field strength averaged over one period of vibration. From equations (3

and (5), Io the intensity of the incident beam and Is the intensity of the scattered beam are obtained. The ratio of these two quantities is,

$$\frac{Is}{Io} = \frac{16\pi^4 \alpha^2 \sin^2 \phi_2}{\lambda^4 r^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

where λ, the wavelength of light in vacuo replaces ξ.

The angular dependence of the scattered light may be seen more clearly from fig. (1). The incident wave is shown as plane polarised in the X Z plane. If the incident beam is unpolarised, the scattering will consist of two polarised components. Ioy = Ioz polarised along the Y and Z directions, then Io=Ioy+Ioz and the total scatter Is=Iy+Iz will be given by

$$\frac{Is}{Io} = \frac{8\pi^4 \alpha^2}{r^2 \lambda^4} (\sin^2 \phi_1 + \sin^2 \phi_2) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

The last factor is equal to $(1+\cos^2\theta)$ so the scattering at 90° is wholly plane polarised and increases symmetrically with θ to twice the value at $\theta=0°$ and 180° when the polarization vanishes. This is true only as long as the

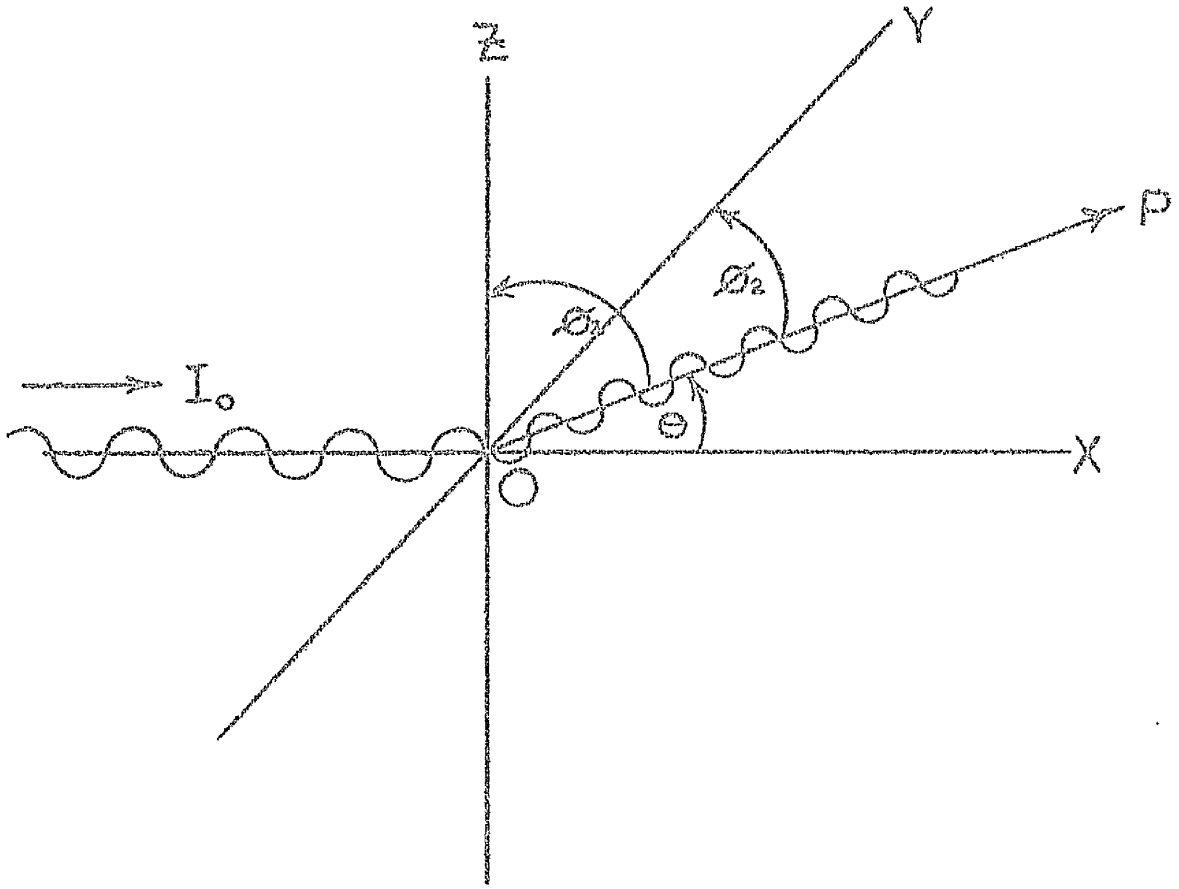


FIG I.

particles are completely isotropic. When the scattering particles are anistropic, the scattering at 90° is no longer completely vertically plane-polarised but reinforced by an additional horizontal component. The ratio of the horizontal to vertical component is called the depolarisation $\rho = \frac{I\,h}{I\,v} = \frac{I\,vh + I\,hh}{I\,vv + I\,hv}$. here e.g. I vh is the horizontal component of the scattered light caused by the vertical component of the incident light etc. Cabannes (48) has evolved a correction factor $f_\rho = \frac{6-7\rho}{6+6\rho}$ to be included in the final equation to account for depolarisation. For solutions the depolarisation is usually rather strongly dependent on the concentration, indicating interaction between the solute particles. Consequently, there is no theoretical reason for applying the Cabannes factor to scattered intensities at finite concentrations. The correct method is to extrapolate ρ to zero concentration, calculte f_ρ at C=0 and apply this correction to the molecular weight. In the detergents studied in this investigation the observed depolarisation is small and f_ρ varied from 0.95 to unity.

In almost all cases it was consequently neglected in the final analysis.

It can be shown that $\varepsilon-1=4\pi N\alpha$ where ε is the dielectric constant and N the number of molecules per c.c. Also from Maxwells electromagnetic equations $\varepsilon=n^2$ where n is the refractive index of the material

$$n^2-1 = 4\pi N\alpha \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

Fluctuation Theory of Light Scattering. The solution may be divided into elements of volume δV, whose linear dimensions are small compared with the wavelenght of light, of which there are N per c.c. i.e.

$$N\delta V = 1 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

The variable of composition is C^1 the concentration of solute averaged over all the solution. The fluctuating concentration C in a volume element may be written as

$$C = C^1 + \delta C.$$

where δC may be positive or negative. Due to this fluctuation in concentration there will be fluctuations in the polarisability α.

$$\alpha = \alpha^1 + \delta\alpha$$

Substituting in equation (6) for α we obtain the equation for scatter from such a volume element.

$$\frac{Is}{Io} = \frac{16\pi^4 (\alpha^1 + \delta\alpha)^2 \sin^2\phi_1}{\lambda^4 r^2} \quad \ldots\ldots\ldots\ldots(10)$$

Expanding $(\alpha^1 + \delta\alpha)^2$, the only term which is unique to the solution is $\delta\alpha^2$ and since $N = \frac{1}{\delta V}$

$$\frac{Is}{Io} = \frac{16\pi^4 \overline{\delta\alpha^2} \sin^2\phi_1}{\lambda^4 r^2 \delta V} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

$\overline{\delta\alpha^2}$ is the average value of $(\delta\alpha)^2$ for a large number of elements at any instant.

$$\delta\alpha = \left(\frac{\delta\alpha}{\delta p}\right)_{T,C} \delta p + \left(\frac{\delta\alpha}{\delta T}\right)_{pC} \delta T + \left(\frac{\delta\alpha}{\delta C}\right)_{T,p} \delta C \quad \ldots\ldots\ldots\ldots(12)$$

Again for solution as opposed to solvent only

$\delta\alpha = \left(\frac{\delta\alpha}{\delta C}\right)_{T,p}$ C is unique to the solution since the scatter from the solvent is subtracted from that of the solution. Using equation (8).

$$\left(\frac{\delta\alpha}{\delta C}\right)_{Tp} = \frac{\delta V}{2\pi} n \left(\frac{dn}{dC}\right)_{Tp} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

From equation (11) and (13)

$$\frac{Is}{Io} = \frac{4\pi^2 \delta V n^2 \frac{dn}{dc}^2 \sin^2 \phi_1}{\lambda^4 r^2} \cdot \frac{}{(\delta C)^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

where $\overline{(\delta C)^2}$ is the average value of $(\delta C)^2$. This quantity depends on the way the Gibbs Free Energy of the solution varies with concentration. It can be shown that,

$$\overline{(\delta C)^2} = \frac{kT}{\left(\frac{\delta^2 G}{\delta C^2}\right)_{T,p}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (15)$$

where k is Boltzmann's Constant and G is the Gibbs Free Energy.

If n_1 and n_2 are the number of moles of solvent and solute respectively in a volume δV and $\overline{V_1}$ and $\overline{V_2}$ are the partial molal volumes, then,

$$n_1 \overline{V_1} + n_2 \overline{V_2} = \delta V.$$

By definition $dG = \mu_1 dn_1 + \mu_2 dn_2$ where μ_1 and μ_2 are the chemical potentials of solvent and solute respectively; and M the molecular weight.

$$\left(\frac{\partial G}{\partial C}\right)_{T,p} = \left(\mu_2 - \frac{\overline{V_2}}{\overline{V_1}} \cdot \mu_1\right) \cdot \frac{\delta V}{M}$$

Differentiating ;

$$\left(\frac{\partial^2 G}{\partial C^2}\right)_{Tp} = \frac{\delta V}{M}\left[\left(\frac{\partial \mu_2}{\partial C}\right)_{Tp} - \frac{\overline{V_2}}{\overline{V_1}}\left(\frac{\partial \mu_1}{\partial C}\right)_{T,p}\right]$$

By the Gibbs Duhem equation,

$$n_1 d\mu_1 + n_2 d\mu_2 = 0.$$

$$\therefore \quad \left(\frac{\partial^2 G}{\partial C^2}\right)_{Tp} = -\frac{\delta V}{M}\left(\frac{\overline{n_1 V_1} + \overline{n_2 V_2}}{\overline{n_2 V_1}}\right)\left(\frac{\partial \mu_1}{\partial C}\right)_{T,p} \quad \ldots(16)$$

and since $\dfrac{n_2 M}{\overline{n_1 V_1} + \overline{n_2 V_2}} = C$,

$$\text{then} \quad \left(\frac{\partial^2 G}{\partial C^2}\right)_{T,p} = -\frac{\delta V}{C\,\overline{V_1}}\left(\frac{\partial \mu_1}{\partial C}\right)_{T,p} \quad \ldots\ldots(17)$$

Substituting in equations (14) and (15)

$$\frac{I_2}{I_0} = \frac{2\pi^2 \cdot n^2\left(\frac{dn}{dc}\right)^2 \cdot (1 + \cos^2\theta)\, C}{\lambda^4 r^2\left[-\frac{1}{\overline{V_1}\,RT}\left(\frac{\partial \mu_1}{\partial C}\right)_{T,p}\right]}$$

where θ is the angle between the incident and scattered beams.

The equation relating chemical potential to concentration may be written as :-

$$\mu_1 - \mu_1^{\circ} = - RT\, V_1^{\circ} C \left(\frac{1}{M} + BC + C'C^2 + \right) \quad \ldots\ldots(19)$$

where C is the concentration of the solute of molecular weight M. Differentiating wrt. C:-

$$\left(\frac{\partial \mu_1}{\partial C} \right)_{Tp} = - RT\, V_1^{\circ} \left(\frac{1}{M} + 2BC + 3C'C^2 + \ldots \right)$$

If $V_1^{\circ} = \overline{V_1}$ in dilute solution ,

$$\frac{Is}{Io} = \frac{2\pi^2 n_o^2 \left(\frac{dn}{dc} \right)^2 (1 + \cos^2\theta).C}{N \cdot \lambda^4 r^2 \left(\frac{1}{M} + 2BC + 3C'C^2 + \ldots \right)} \quad \ldots\ldots\ldots\ldots\ldots\ldots(20)$$

Since $n_o^2 \approx n^2$ for dilute solutions, the usual way of representing this equation is to define the quantity

$$Re = \frac{Is r^2}{Io\,(1 + \cos^2\theta)}$$ as the Rayleigh Ratio and

write $$\frac{KC}{Ro} = \frac{1}{Mr} + 2BC + 3C'C^2 + \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(21)$$

Application to Detergent Solutions:- The first to indicate the applicability of the light scattering method to detergent solutions was Debye (29,49). He modified equation (21) by using the turbidity factor τ, which is essentially the extinction coefficient in cm^{-1} due to the fluctuations in concentration; and $I = I_0 e^{-\tau \ell}$, ℓ is the optical path length through the scattering medium.

It can be shown (49) thats for R_{90}.

$$\tau = 2\pi \int_0^{\pi} \left(I_\Theta \frac{r^2}{I_0} \right) . \sin \theta . d\theta \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (22)$$

$$\tau = \frac{16\pi}{3} . R_{90}$$

Hence equation (21) may be written in the form

$$\frac{H\,C}{\tau} = \frac{1}{M_a} + 2BC \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (23)$$ where

$$H = \frac{32\pi^3 n_0^2}{3 N \lambda^4} \left(\frac{dn}{dc} \right)^2$$

The second virial coefficient B is a measure of the deviation from ideality. In very dilute soap solutions the scattering is no greater than that of water but on raising the concentration above C_2 (the C.M.C.) the turbidity rapidly increases. By replacing the concentration term C by (C-Co) and plotting the reduced turbidity $\frac{H(C-Co)}{\tau}$ against (C-Co) Debye found that linear plots can be obtained, the intercept of which gives $\frac{1}{Mn}$, the reciprocal of the micellar weight. This is equivalent to regarding the solution at the C.M.C. as the solvent and the concentration of soap in excess of the C.M.C. as the solute. This treatment cannot be considered as complete since it deals with micelles as if they were uncharged polymers.

Recently, Mysels (50,51,52) and Hutchinson (53) have elaborated the theory somewhat further by trying to calculate the effect of charge on the micelles. Hutchinson, while recoguizing that the micelle is charged in water, believes that it becomes uncharged in aqueous salt solutions. For

uncharged micelles the effect of the monomeric ions may be lumped with that of the solvent and neglected in the calculation of micellar weights. Mysels, on the other hand, points out that the micelle of ionic surfactants is in fact highly charged both in water and in the presence of salt, as shown by its high electrophoretic mobility. He argues that the charge tends to reduce the extent of the fluctuations, that the presence of monomeric ions reduces the optical efficiency of the fluctuations and that the equilibrium between monomeric ions and charged micelles affects the concentration of monomer beyond the C.M.C..

Probably the most lucid and complete treatment of light scattering in detergent solutions, taking account of the effect of charge on the micelles, was provided by Prins (54) in his study of some long chain sodium alkyl - 1 sulphates. Some of his theory is outlined below:-

He assumed that the degree of association n is the same for all micelles (i.e. a narrow distribution). In view of the fact that the electrical double layer around the micelles consists mainly of an excess of counter ions he assumes that a fraction $(1-p/_n)$ of the counter ions is 'bound' to the micellar surface.

These counter ions do not contribute independently to the light scattered since their fluctuations are very small due to the strong field round the micelle.

After applying the general multicomponent fluctuation theory, along similar lines to that presented earlier but with the added complication of charge, he obtains the following equation.

$$\frac{H(C-Co)}{\tau} = \frac{1}{Mn^{*}}\left[1 + \frac{C-Co}{2nC\sigma}\left(p(p+1) - p/b_1\right) + \right] \ldots\ldots\ldots (24)$$

where $Mn^{*} = Mn\ b_1$ and $b_1 = (1 + \alpha^2/2 - \alpha)$, and $\alpha = p/n$. H, Co, C, τ and Mn have already been defined.

In the case p equals zero we have a completely uncharged micelle and (24) reduces to the well known formula:

$$\frac{H(C-Co)}{\tau} = \frac{1}{Mn}$$

The fact that $\frac{H(C-Co)}{\tau}$ versus $(C-Co)$ is usually a straight line in dilute solutions is substantial evidence in favour of an ideal monodisperse micelle equilibrium. The intercept and slope of this line give two equations for p/n which may then be determined separately.

Further complications arise with the addition of a salt to the micellar solution.

If N_1 = co c. of monomer ions; No = conc. of water molecules; $N_2 c_0 n_0$ of salt ions added; Mn = no. of micelles; n_s the refractive index of the salt solution and n_1 the refractive index of the detergent solution; $k = \frac{n_s}{n_1}$; b_1 as before; and $b_s = (1+k^2\alpha^s - 2k\alpha)$ $\lambda_1 = 2N_1 b_1 + N_s b_s$

Prins evolved the following equation.

$$\frac{H(C-Co)}{\tau} = \frac{1}{Mn^*}\left[1 + (C-Co)\left(p(p+1) - \frac{p(2N_1+N_s)}{\lambda_1}\right) - \frac{No\,n_0(N_1+nN_n)}{(2N_1+N_s)\,Mn} + \ldots\right] \quad \text{where } Mn^* = \frac{Mn\lambda_1}{(2N_1 + N_s)} \quad \ldots\ldots(25)$$

When salt is added to a solution with a low C.M.C. ($=N_1$) the salt concentration Ns soon becomes much larger than the monomer concentration N_1 . Eq. (25) then takes the simpler form:

$$\frac{H\,(C-Co)}{\tau} = \frac{1}{Mn^*}\left[1 + (C-Co)\left(p(p+1) - \frac{p}{b_s}\right)\frac{M_s}{C_s Mn} + \ldots\right] \quad \ldots\ldots(25)$$

where M_s is the molecular weight of the salt and C_s the conc.

As in the preceeding case it is possible to determine p and n separately from a combination of intercept and slope. Beyond a certain salt concentration it is found, experimentally, that the slope is practically zero i.e. that p = 0 in the above equation. In this case the intercept gives the correct micellar weight. Prins applied a further correction that is needed for micellar solutions caused by the restriction in freedom of the micelles as a result of double layer repulsion. This gives the micelles an apparent volume much greater than their actual one. The effective diameter D is determined by the condition that the electrostatic repulsion of the double layers equals kT, when the distance between the two centres is D. The volume excluded per micelle is found to be $\psi = 4\pi D^3/3$.

Inserting the above term in the equation for the system water-micelles-monomer gives.

$$\frac{\pi(C-Co)}{\tau} = \frac{1}{b_1 M_n} + \left[\left(\frac{(p(p+1) - p/b_1)}{2n_1 Co b_1 M_n} + \frac{8\sqrt{n_1 N}}{b_1 M^2 n} \right) \times (C-Co) + \cdots \right] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (27)$$

where $\nu n = 4\pi \left(\frac{D}{2}\right)^3$ N = total number of detergent molecules.

From this result it is seen that the slope of $\frac{K(C-Co)}{\tau}$ versus (C-Co) is determined by a 'charge' term and an excluded volume term. By assuming somewhat arbitary values of p = 10 and n = 100 for dodecyl sulphate Prins calculated that the excluded volume term is smaller than the charge term but that its omission is not allowed. This leads to the conclusion that it is impossible to measure p and n separately from light scattering data above as suggested earlier, because a separate calculation of νn requires a knowledge of the ζ potential of the micelle (Stigter (55,56) has found a means to calculate the effective diameter D from the ζ potential of the micelle by applying the tables of Verwey and Overbeek (57) modified in such a way as to make them valid for rather small spherical particles with a high surface potential (58)). Using this more or less reliable estimate of the excluded volume term it is possible to evaluate p and n from the intercept and slope of the light

scattering curve. An approximately correct value for D may be obtained in the following way. The actual radius r of the supposedly spherical micelle may be estimated from the apparent degree of association by assuming a density of 1.2 for the micelles. Using the reciprocal characteristic length K of the Debye-Huckel theory to estimate the double layer thickness we get $D = 2r + \frac{2}{K}$. For dodecyl sulphate the more correct value as computed by Stigter (55) yields 113A° for D while this approximation gives 111A°. The same close correspondence is found for D values on addition of salt.

One of the most important conclusions to be drawn from Prins theory is that it contradicts, indeed disproves, the theory of Hutchinson (53), who argued that the experimentally observed changes in Mn on addition of electrolyte may be completely due to a decreasing 'degree of ionisation' of the micelles. From the evaluations of p and n and using the approximate D values as calculated above, Prins showed quite definitely that Hutchinsons statement is incorrect; the change in Mn being mainly due to a change in the degree

of aggregation accompanied by an increase in micellar size.

Purpose of this Work:- As indicated by the rather involved theory presented above, light scattering in solutions of colloidal electrolytes is far from straight forward. The principal difficulties are ;

(1) from an experimental point of view $\frac{H\,(C-Co)}{\tau}$ must be accurately evaluated at low values of C in order to obtain the correct value of the intercept at the C.M.C. Co.. Unfortunately, it is precisely in this region that errors in $\frac{H(C-Co)}{\tau}$ are the largest owing to uncertainties in the exact value of the C.M.C., the very low turbidities involved and the dissociation of micelles at the C.M.C.,

(2) the ionic nature of the micelles. As well as the theoretical considerations of Frins the fact that added electrolytes affect the size of the micelles of colloidal electrolytes, but have no effect at all on the non-ionic detergents, shows the importance of the electric term in

the former case.

(3) the possibility that the micellar size does not remain constant as the concentration is varied. Instead of altering the theory, which is still inadequate, to try and understand the complexity of micelles in dilute solution the suggestion that it may be possible to modify the solutions in such a way as to eliminate some of the difficulties and allow for a more concise analysis in the light of present theory was proposed. This could be achieved by utilizing unsaturated soaps such as sodium oleate $CH_3(CH_2)_7CH = CH(CH_2)_7\ COO^-Na^+$, undecenyl trimethyl ammonium bromide (U.T.A.B.) $CH_2=CH(CH_2)_9 N^+(CH_3)_3Br^-$ and sodium undecenyl sulphate (S.U.S.) $CH_2=CH(CH_2)_9OSO_3^-\ Na^+$. By initiating polymerisation of the double bonds of the molecules in each separate micelle a 'polymicelle' may be obtained. A solution containing such micelles would escape difficulties (1) and (3), there being ideally no dissociation at the theoretical C.M.C.. Case (2) could be overcome for the carboxylic soaps by acidification after polymerisation and extraction of the polymicellar substance by ether when it could be investigated in an organic

solvent as an ordinary polymer. Although not entirely successful in its original conception the idea was fruitful in that it was found that 'polymicelles' could be formed and the results and discussion of light scattering in such solutions are presented.

EXPERIMENTAL.

Preparation of the Detergents:- Recent work on light scattering (21) has underlined the importance of working with pure detergents. The presence of foreign materials can considerably modify the properties of micelles, especially in dilute solution not far removed from the C.M.C.. Indeed a lot of the published data on the general properties of detergent solutions has been made on impure and therefore irreproducible detergents. Considerable care was therefore taken in the purification of the commercially available detergents and in the synthesis of the new compounds.

Preparation of Sodium Oleate :- Sodium oleate was chosen from a series of unsaturated fatty acid soaps being the cheapest and most easily available. Two samples were employed. The first was a commercial one from Hopkins and Williams, purified by recrystallisation from dry ethanol and vacuum dried. The other sample was prepared by neutralising oleic acid (Fluka purissa) in ethanol with sodium ethoxide.

$$2Na + 2EtOH \longrightarrow 2Na^{+}\,OEt^{-} + H_2$$

$$CH_3(CH_2)_7CH = CH(CH_2)_7COOH + Na^{+}\,OEt^{-} \longrightarrow RCOO^{-}\,Na^{+} + EtOH$$

Best results were obtained by using a slight excess of the ethoxide (measured by phenophthalein indicator), otherwise the product tended to be oily due to unreacted oleic acid. The reaction took place at room temperature, and the white crystals of sodium oleate were recrystallised from dry ethanol and subsequently vacuum dried. This sample gave the following micro analysis.

	%C	=	71.4	%C	= 72
ACTUAL	%H	=	11.3	THEORETICAL %H	= 11.33

Preparation of Sodium Undecenyl Sulphate:- This compound was prepared by reacting chloro-sulphonic acid with the unsaturated alcohol undecen-1-ol (Fluka puriss)

$$CH_2 = CH(CH_2)_8CH_2OH + ClSO_3H \xrightarrow[\text{acid}]{\text{acetic}} CH_2 = CH(CH_2)_8CH_2OSO_3^{-}H^{+}$$

$$\downarrow$$

Na salt

25 gms. acetic acid and 17 gms. chlorosulphonic acid were introduced into the reaction vessel at 0-5°C with stirring.

25 gms. undecen-1-ol was added gradually over a 30 min. period and the whole mixture stirred for a further 30 min. at 4°C. Subsequently the reaction mixture was poured onto 100 gms. of crushed ice; 75 gms. of n butanol added and the solution neutralised with 2N sodium carbonate solutions and solid $NaHCO_3$ to keep it saturated with inorganic sodium salts.

The neutral sodium alcohol sulphate was separated with the butanol layer, the aqueous layer being further extracted with four successive portions of butanol. By concentrating the butanol extracts under vacuum the water was removed and the precipitated inorganic salts separated by filtration. The solution was then distilled with azeotropic removal of the butanol, by adding water towards the end of each distillation. After all the butanol had been removed the pH was adjusted to 7 and the solutions extracted throughly with ether to remove any unsulphonated substance. The ether in the aqueous solution was removed by concentration under vacuum and the solution of sodium undecenyl sulphate, thus obtained evaporated to dryness in a vacuum oven. After

recrystallisation three times from dry acetone micro analysis on the compound gave:-

ACTUAL		THEORETICAL	
%C = 50.33		%C = 51.5	
%H = 8.1		%H = 8.2	

Preparation of Undecyl Trimethylammonium Bromide:- This detergent was prepared by reacting 1 brom-undecane (Fluka purum) with trimethylamine at 0°C.

$$CH_3(CH_2)_9CH_2Br + N(CH_3)_3 \longrightarrow CH_3(CH_2)_9CH_2N(CH_3)_3^{+}\ Br^{-}$$

The trimethylamine was distilled from a 33% alcoholic solution under vacuum. It was allowed to bubble via an inverted filter funnel through the 1 brom-undecane at 0°C. The product was separated by filtration through a No. 3 sinter glass filter, recrystallised twice from dry acetone and stored in a dessicator. Purity of the compound was checked both by micro analysis and by the Mohr titration. This involves adding ethanol to a solution of the detergent of known concentration to break down the micelles such that it behaves like a weak-1-1 electrolyte. Titration with silver nitrate gives a well defined end point using dichlorofluoresein as an absorption

indicator. This enables a check to be made on the purity of the compound w.r.t. bromine content.

Micro analysis gave;

ACTUAL	%C	= 55.83	THEORETICAL	%C	= 51.2
	%N	= 11.15		%N	= 11.0

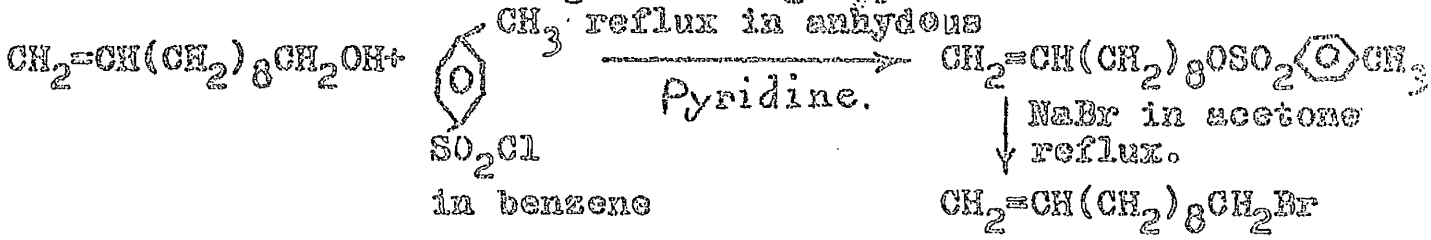
MOLE TITRE. 98.6% pure w.r.t. Br.

The discrepency between the actual and theoretical carbon percentages may be due to a bad analysis as the soap appears to be acceptably pure w.r.t. hydrogen and bromine contents. Also the light scattering runs did not indicate the presence of extraneous impurity, so the soap was considered to be as pure as was experimentally possible to prepare.

Preparation of Undecenyl Trimethyl Ammonium Bromide.

The preparation of the unsaturated bromide from undecen-1-ol presented some difficulty. Conventional means of bromination had to be avoided since any excess of HBr would lead to bromination of the C=C double bond. An attempt was

made to protect it by sulphonating the alcohol before bromination thus rendering the end group more reactive.



The resultant compound however did not give a satisfactory I.R. spectroanalysis (comparing the C=C peaks with the original alcohol). After a few attempts this approach was abandoned and a more direct method sought. The most successful involved the use of PBr_3 in slight excess, refluxed in dry benzene with the alcohol. The resultant mixture was poured into ice water to remove the excess as $P(OH)_3$, extracted with ether and dried with anhydrous Na_2SO_4. Removal of the ether and benzene by vac. distillation left a clear viscous liquid which gave a positive bromine test and an I.R. trace with similar C=C peaks to its parent alcohol.

As with its saturated counterpart the alkyl bromide was reacted at 0°C with trimethylamine to give undecenyl trimethylammonium bromide which was recrystallised from dry acetone.

The reactions may be summarised by :—

$$3CH_2{=}CH(CH_2)_8CH_2OH \xrightarrow[\text{reflux in benzene.}]{PBr_3\ X'S} 3CH_2{=}CH(CH_2)_8CH_2Br + P(OH)_3.$$

$$CH_2{=}CH(CH_2)_8CH_2Br \xrightarrow[0°C]{(CH_3)_3N\ X'S} CH_2{=}CH(CH_2)_8CH_2\overset{+}{N}(CH_3)_3\overset{-}{Br}$$

The micro analysis of this compound gave good agreement with theoretical percentages and the Mohr titration indicated a product 97.6% pure w.r.t. bromine content.

Clarification of Water:- It is of paramount importance that the water used in the preparation of the detergent solutions is optically clear and as 'dust free' as is experimentally possible. Any foreign material present in the water solvent will immediately be solubilized by micelles thus affecting their properties. Although organic non-polar liquids are relatively easy to clarify by filtration through ultrafine sintered pyrex glass filters, the affinity of dust particles for water is comparable with that of glass making clarification by the use of glass filters none too satisfactory. A good measure of the cleanliness of a solution or solvent is by

determining the dissymmetry of the light scattered in it. Dissymmetry occurs when the particle which is scattering light has a dimension comparable with the wavelength of light used, in which case interference occurs between the light waves scattered from different parts of the particle. The result of this is to reduce the intensity of light scattered at any angle θ other than $\theta = 0$. The dissymmetry $P(\theta)$ is defined by $P(\theta) = \frac{I\theta}{I(180^\circ - \theta)}$ in this case $\frac{I\,45^\circ}{I\,135^\circ} = P(\theta)$. Any observed dissymmetry in water must therefore be due to suspended dust particles. By measuring the scattered intensities at 45°, 135° and 90° for various water samples purified in different ways the most satisfactory method was selected on the basis of the lowest dissymmetry and the lowest scatter at 90°.

The dissymmetry and I_{90} values tabulated below are averaged over a number of water samples.

Water Sample.	I_{45° / I_{135°	I 90 Arbitrary Units.
A Distilled	2.1	13.1
B Deionized	2.5	15.2
C Distilled and centrifuged	1.12	10.9
D Distilled and passed through millipore filter	1.07	10.5
E Deionized and passed through millipore filter	1.08	10.6

Millipore filters consist of a cellulose ester membrane through which the water is forced, preferably by applying pressure above the filtering membrane. As is apparent there is little to choose between the last three techniques, the dissymmetry being close to unity in each case. Since a large quantity of water was required method E was eventually chosen. Filtration can be made a continuous process while centrifugation has to be done in batches and is much more tedious. Deionization was carried out on an ion exchange column.

It is an experimentally observed fact that dilute salt solutions are more easily cleaned than pure water. The intensity of scatter from a number of K Br solutions which had been clarified by centrifugation was plotted against concentration. Extrapolation of this graph to zero salt concentration gave a value of $I_{90} = 9.9$ for pure water. Indeed the solvent scatter for some of the runs often came close to this value which was considered to be the limit of 'cleanliness' which could be obtained.

Conductivity and Surface Tension Measurements:- Specific conductivities K for the detergent solutions were measured directly from a Wayne-Kerr Universal bridge using a dipping electrode assembly. Multiplying by the cell constant and dividing by the concentration in equivalents per c.c. gives the equivalent conductance A. The solutions were kept in a thermostatted bath at 25± .1°C and were stirred after each successive dilution until equilibrium had been attained (usually ~15 mins.)

Sugden's (59) improved version of the maximum bubble pressure device was used to measure the surface tension at different concentrations. Two tubes of different radii r_1,

and r_2 were immersed to the same depth in the solution and connected via glass tubing to a manometer and a source of air pressure. The maximum readings p_1 and p_2 on the manometer at the instant when the bubble breaks away from each orifice are recorded. It is easily shown that the following equation holds.

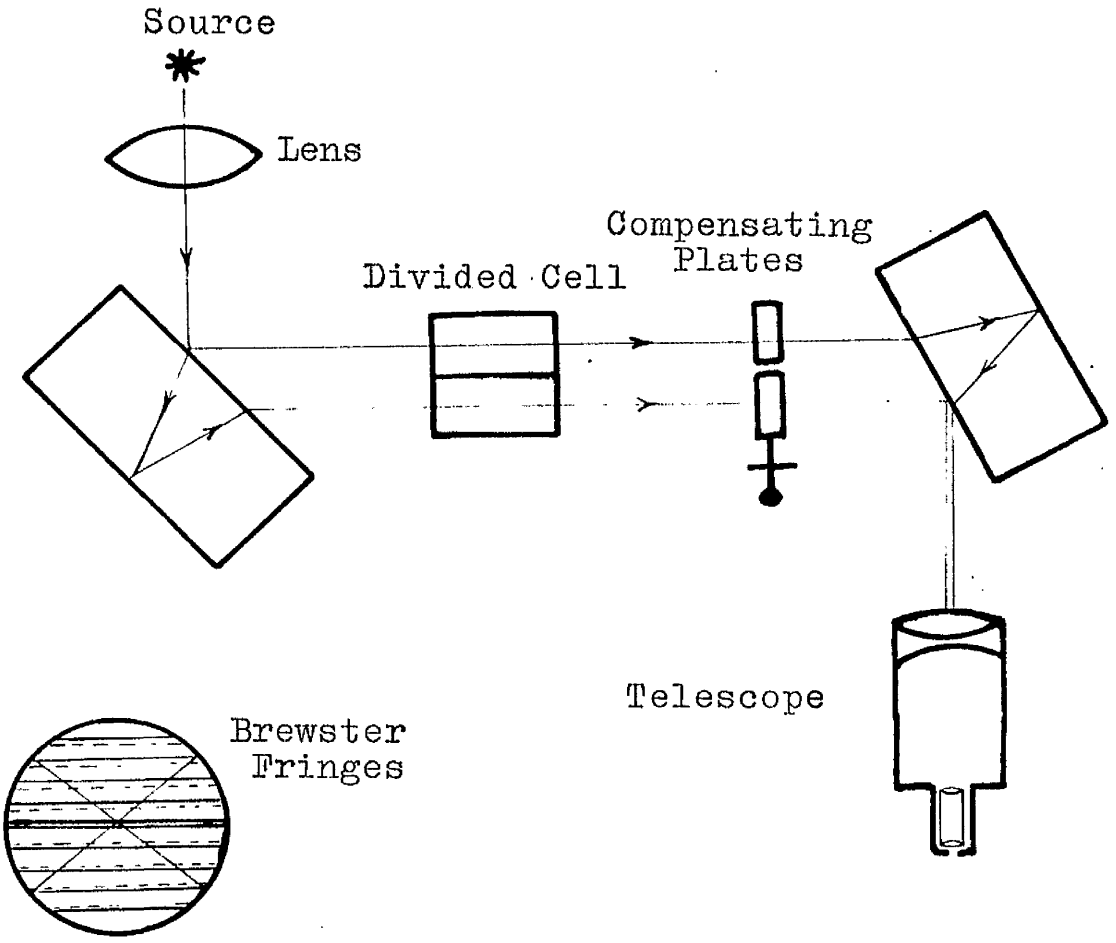
$$\gamma = A(P_1 - P_2)\left(1 + \frac{B\rho}{P_1 - P_2}\right)$$

γ = surface tension.
ρ = density.
A and B are constants.

The apparatus was standardised (i.e. A and B determined) by measurements on liquids of known surface tension(benzene, water and ethanol). The advantage of this method is that it is not necessary to determine the radii of the two tubes as these are incorporated in the constant B.

Refractive Index Increments:- The precision with which molecular weights can be determined by light scattering methods depends greatly on the accurate measurement of the change in refractive index with concentration $\left(\frac{dn}{dc}\right)$, as this appears as a squared term in the Debye equation (23). The Rayleigh and the Jamin Interferometers were employed with

satisfactory results in both cases. In both instruments the quantity measured was the difference in refraction between solvent and solution by interference of a beam of light passing through a divided cell. The calibration of both instruments was made using a standard sucrose solution where $\left(\frac{dn}{dc}\right)$ = 0.1430 at 25°C for concentrations ranging from 0.5 to 4.5 gm/ml. A white light source was used which made the interference pattern of the double slit coloured with the exception of two central black minima. The difference in light path between the two compartments can be compensated for by a movable plane parallel glass plate in such a way that the two black minima shift back to the zero position above the reference interference pattern. The number of fringes traversed in doing this can be counted by inserting a green filter to wipe out the interference colour. Interpolation of the band shift correct to a fraction of a band enables the refractive index increment between solution and solvent to be calculated.



JAMIN INTERFEROMETER

The bands move according to the following relation.

$$(n_1 - n_2) = \frac{m\lambda}{L}$$

where m = number of fringes that pass a given point in the field.

L = internal width of the cells.

λ = wavelength of the light employed.

n_1, n_2 = refractive index of solution and solvent respectively

$$(n_1 - n_2) = \Delta n$$

A band shift of about 15 is desireable and a number of preliminary tests with the solutions to be measured gave approximately the requisite concentration to produce this shift. This was followed by an accurate determination of $\left(\frac{dn}{dc}\right)$ at the predetermined concentration. Although the temperature coefficient of the refractive index increment is extremely small (Price and Kalwer (60) found $\left(\frac{dn}{dc}\right)$ decreased by 0.2% per C° rise in temp.) the cell was enclosed in a constant temperature unit (25°C) to avoid thermal differences between solvent and solution. A protective covering was designed

to seal the divided cell for using methyl ethyl ketone as solvent to avoid evaporation from the solution with a consequent continuous change in concentration.

Clarification of the Solutions:- As already mentioned it is imperative that liquids investigated by light scattering are free from dust particles. The effect of dust is most noticeable in solvents of low refractive index e.g. water and ethanol since there is a comparatively large value of $\left(\frac{dn}{dc}\right)$ for the dust particles. This is unfortunate because these polar solvents are more difficult to clean than e.g. methyl ethyl ketone or benzene.

Two methods for the clarification of the detergent solutions were adopted. Millipore filters were successfully used in the clarification of the water solvent. Although dissolved by many organic solvents these cellulose ester membranes can be used for aqueous solutions. The filter membrane is clamped between the container for the solution to be filtered and a sinter glass support forming the base. Pressure is applied above the surface of the solution allowing

the filtrate to run directly into the scattering cell. The millipores were washed twice with the solution requiring filtration to avoid concentration changes caused by previous solutions.

The most common technique for optical clarification of solutions is by centrifugation. The angle head type M.S.E. centrifuge was used for times of approximately an hour at a speed of 16,000 r.p.m. which corresponds to an acceleration of 30,000 times that of gravity. A solution was prepared in a standard flask and diluted by pipetting appropriate volumes of solution and solvent into stainless steel centrifuge tubes. Along with a tube containing roughly the same volume of solvent these were balanced to within 0.1 gm. before being placed in the centrifuge. After rotation, 20 mls. of the clarified solution were transferred to the scattering cells from the 30 mls in the centrifuge tubes by means of a clean pipette. Although results were satisfactory from both of these techniques that of centrifugation was preferred, there

being less danger of contamination of one solution by another. All glassware used in the experimental work was immersed in a chromic acid bath for at least twelve hours before washingwith tap water followed by distilled water and dried in an oven.

Light Scattering Apparatus:- The instrument used is marketed by S.O.P.I.C.A. It is based on an original design developed by Wippler and Scheibling (61). A schematic diagram of the apparatus is shown in fig. (2). The light source is a Philip's S.P. water cooled, high pressure mercury lamp and the green beam of wavelength 5460A°, isolated by filters was employed throughout the investigation. The cylindrical scattering cell is suspended in a bath of pure benzene thus eliminating large refraction effects from its outside surface. The bath can be held at a constant temperature by water pumped from a thermostatically controlled unit. The photomultiplier tube receiving the scattered beam can be automatically set at predetermined angles to the incident beam.

LIGHT SCATTERING APPARATUS.

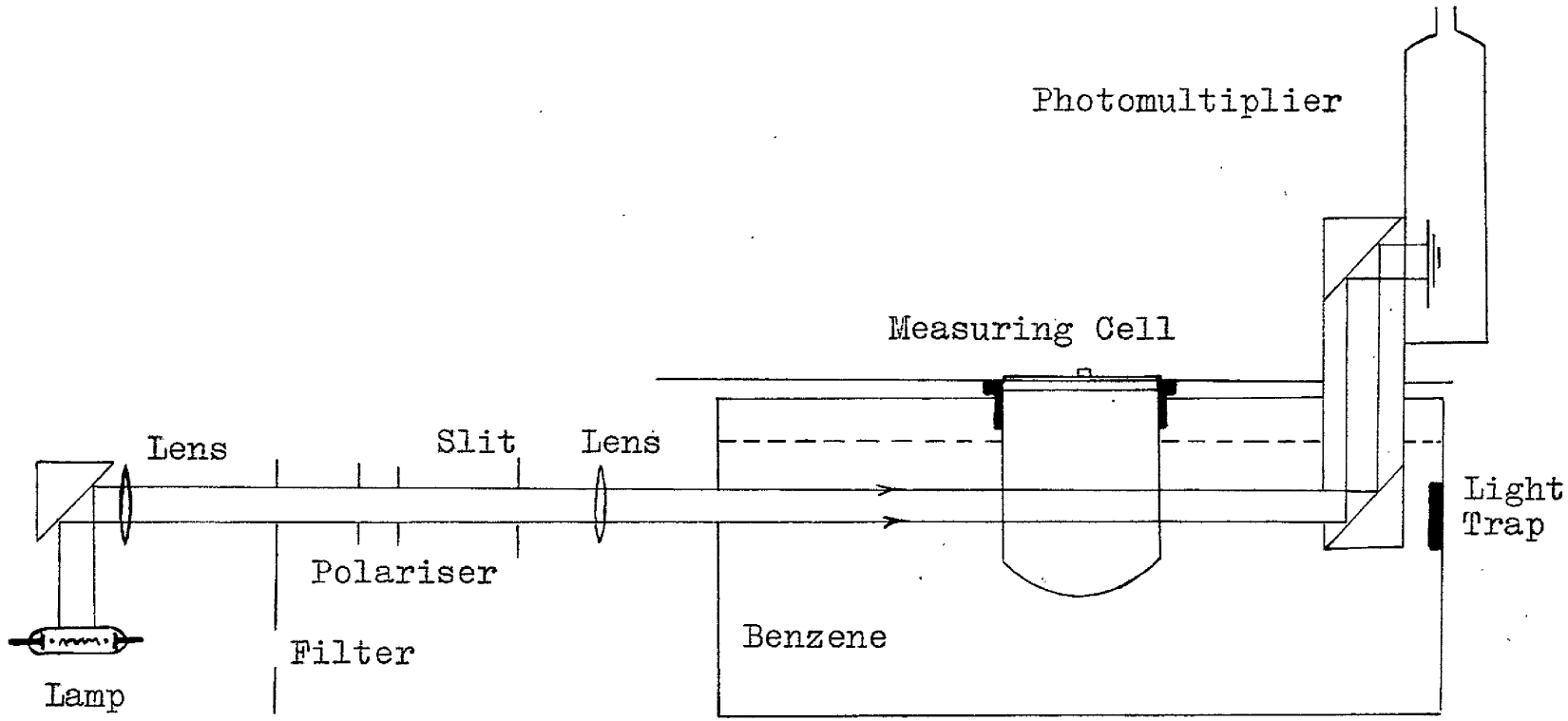


FIGURE 2.

The intensity of the incident beam can be varied by altering the width of the slit S. The intensity is kept constant throughout the investigations by varying the slit such that the scatter from a standard cylindrical glass block is always the same. The glass block is simply a sub — standard calibrated against a dust free sample of pure benzene.

Polymerisation Technique:-

Preliminary work to see whether polymerisation within micelles was possible or not was executed on sodium oleate with and without added styrene. Styrene was pre-polymerised by U.V. light and the pure monomer vacuum distilled from the liquid leaving inhibitor and other impurities behind. The saturation limit for the solubilization of the styrene in 3% sodium oleate solution was estimated by the visible onset of turbidity in a batch of soap-styrene mixtures. The styrene was introduced by a micrometer syringe the amount being easily calculated from a calibration curve of 'distance travelled by the plunger' against weight delivered. Further investigation has revealed that the visible saturation limit may be slightly

higher than the actual limit as determined by spectroscopic methods. This is not critical however since 3/4 of the visible limit was utilised for the polymerisation experiments thus making certain that all the styrene was absorbed within the micelles. It was hoped to prevent an emulsion type polymerisation by using these small quantities with the possibility that the styrene along with the unsaturated soap would enter into the polymerisation mechanism on irradiation.

The best technique for the polymerisations was found by irradiating 3% sodium oleate solutions with and without added styrene and with and without aso bis isobutyro nitrile (A.B.I.N.) as initiator for times of 9,15 and 20 hours and comparing the plots of conductivity of these solutions with the original soap. From the conductivity results, as indicated in the next section the following technique was adopted. Varying amounts of styrene monomer under 0.5 gms. were added to 100 cc. 3% sodium oleate solutions along with 2 crysta s A.B.I.N. ($\sim$ 0.00025 gms.). These solutions were thorougly degased by freezing with liquid N_2 and pumping off on a vacuum line. After irradiation by U.V. light the

solutions were acidified with HCl to convert the sodium salt to pure polymer, which was subsequently extracted with ether. The polymers obtained by vac. distillation of the ether were dis-olved in M.E.K. and their molecules weights determined by light scattering. Limited by the small optimum quantities of styrene added yields were very small but by repeating the process several times enough was obtained for analysis. This difficulty was overcome by using U.T.A.B. and S.V.S. in later experiments as it was found that these detergents could be polymerised with the same initiator and irradiation without the aid of styrene.

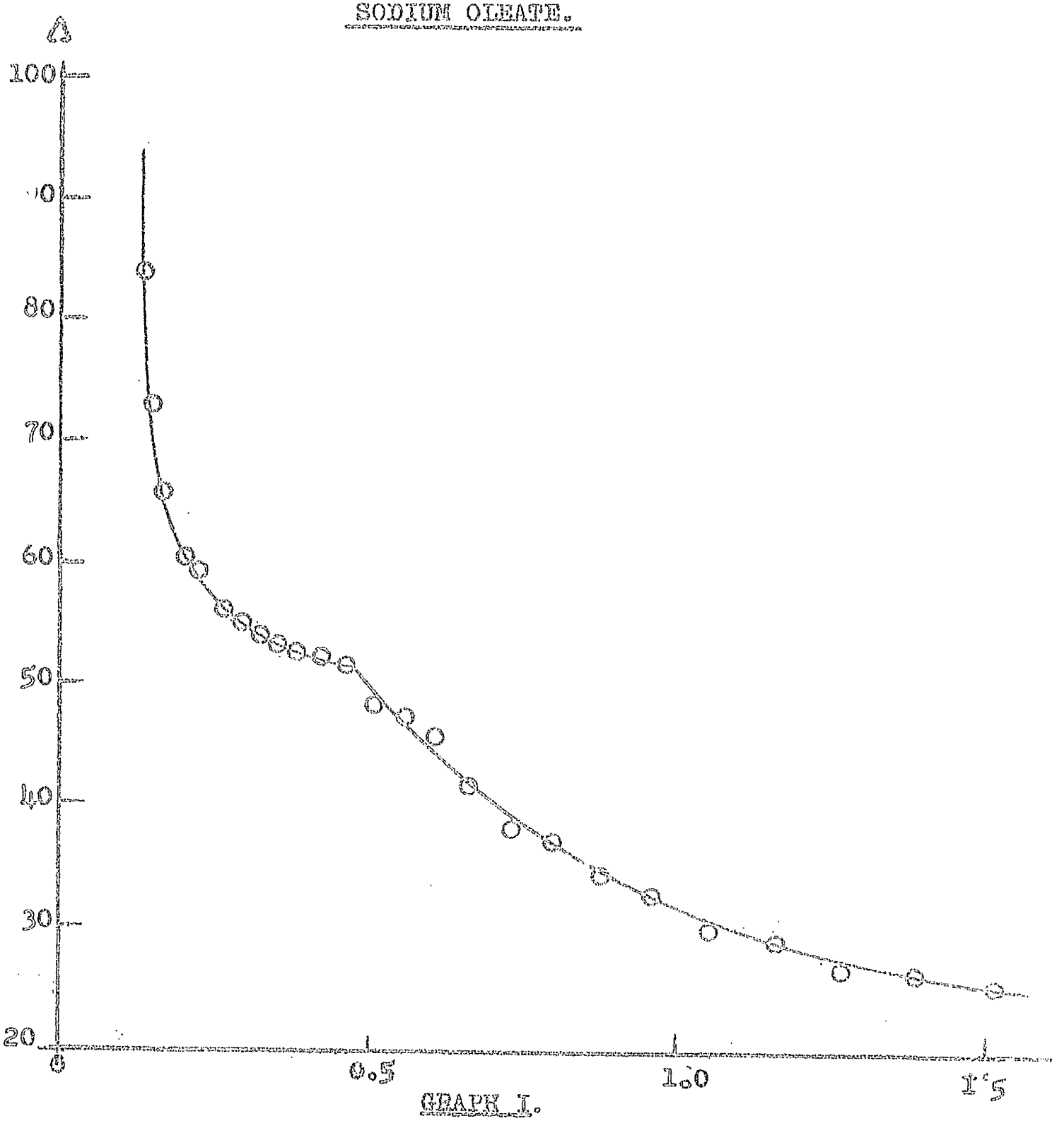
RESULTS AND DISCUSSION.

Initial work on sodium oleate was directed at proving whether or not polymicelles could be formed by U.V. irradiation of a soap solution containing micelles with unsaturated groups in the interior. In order to inquire whether there had been a significant polymerisation of the paraffin chains a comparison was made between conductivity plots before and after irradiation.

In graph I a plot is given of the equivalent conductance Λ at 25°C as a function of the square root of concentration (in moles per litre) for sodium oleate in water. The Λ v's $\sqrt{C}$ curve exhibits a pronounced arrest in Λ commencing at about 0.02M and ending at approximately 0.05M. The rapid increase in conductivity observed below this range can be attributed to hydrolysis of the oleate.

The degree of hydrolysis of a number of fatty acid soaps in water has been measured by Powney and Jordan (62) and it is possible in the region of the arrest that mixed micelle formation occurs between fatty acid molecules (formed by hydrolysis) and soap ions. As the total soap concentration is increased, the ratio of soap ions to fatty acid molecules in the micelle would increase. Ekwall (63) has

SODIUM OLEATE.

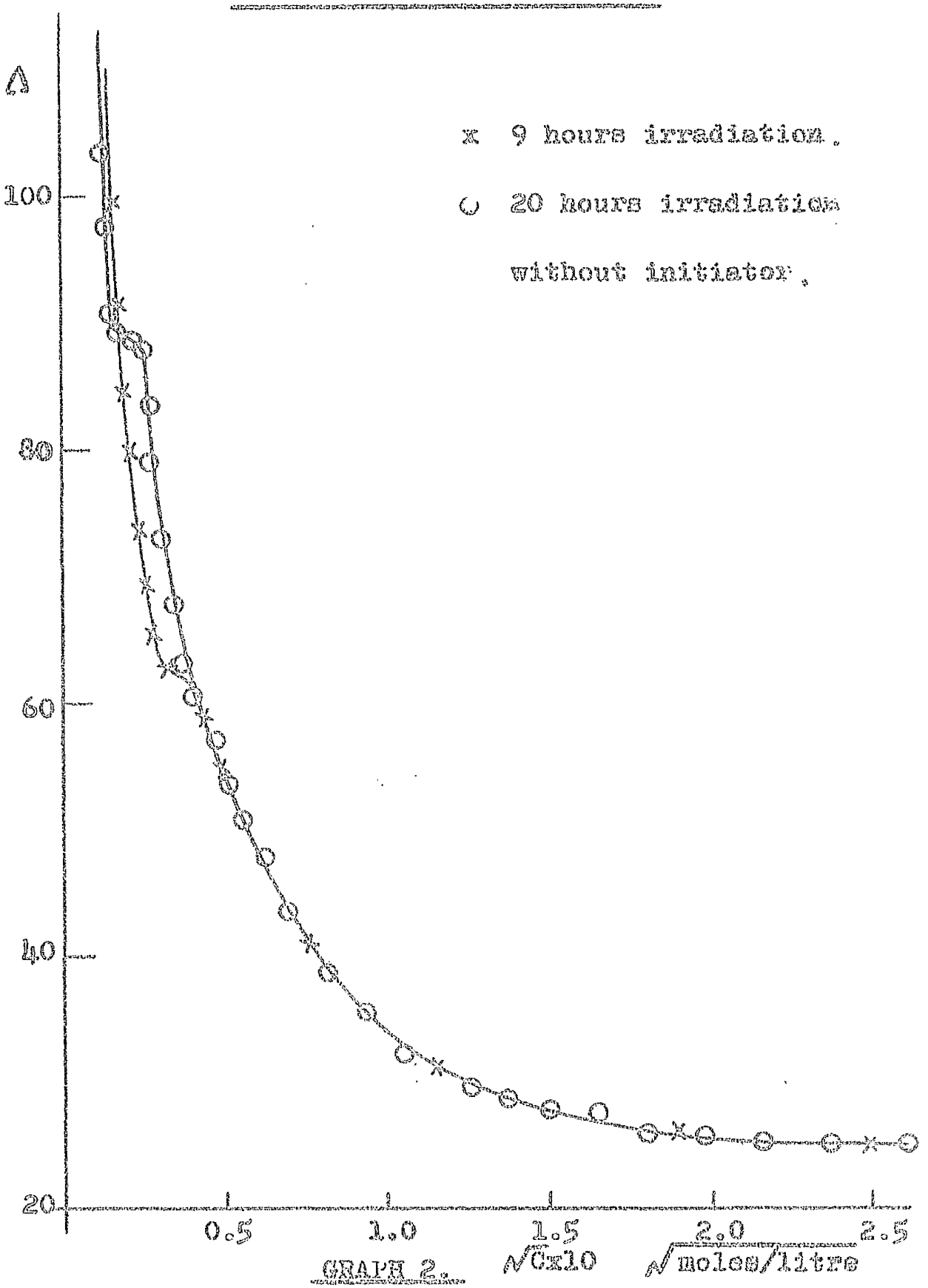


GRAPH I.

observed a similar arrest in the curve for sodium myristate in water. According to this investigator the break can be attributed to the formation of acid soap and the renewed fall at the end of the arrest to colloid formation. In spite of hydrolysis complications it can be said with some certainty that the arrest is due to micelle formation.

If we assume that the paraffin chains of an unsaturated soap micelle can be polymerised together with solubilised styrene then ideally we would expect the break point in the conductivity curve to be eliminated, since there would be no dissociation into single ions at that point. In order to test this theory many experiments were conducted, some of the results of which are summarised in graph 2. It was found that the addition of 0.357 gms. styrene to 50cc. of 3% sodium oleate (approx. ¾ the turbidity limit) gave a Λ Vs $\sqrt{C}$ curve which could be superimposed on the original soap curve. Irradiation of solutions of sodium oleate containing the same amount of styrene, for times varying from 9 to 20 hours

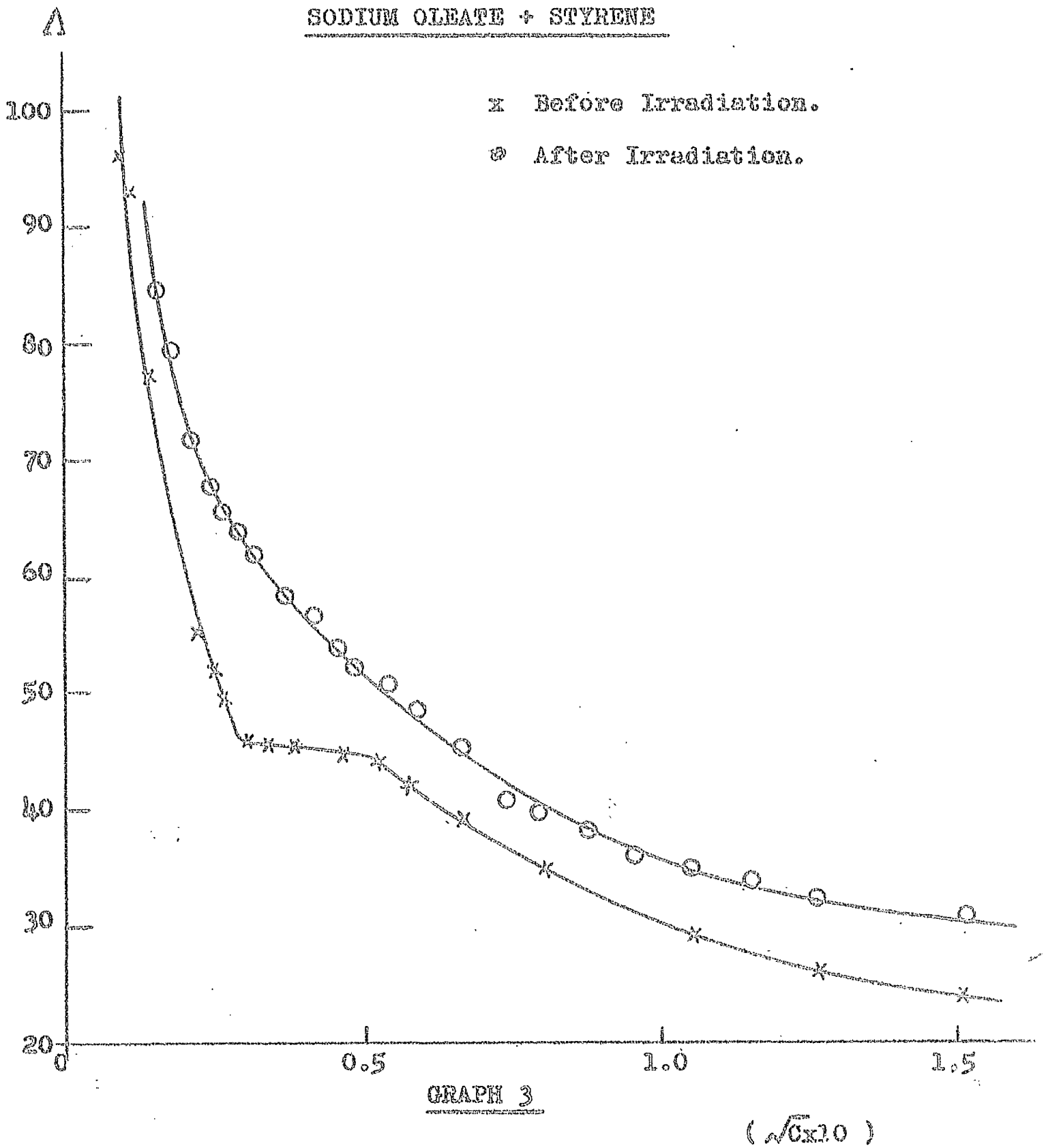
SODIUM OLEATE + STYRENE



GRAPH 2.

still gave rise to an arrest in the Λ v's $\sqrt{C}$ curves but this seemed to be shifted to regions of lower concentration. Before each irradiation the solutions were thoroughly degassed as absorbed oxygen acts as an inhibitor to styrene type polymerisations. If adequate oxygen is present peroxide formation takes precedence over polymerisation and free radicals, which would normally initiate chains, react with oxygen instead. Neuch (64) has suggested that many of the observed anomalies during emulsion polymerisation are due to variations in the dissolved oxygen content of the water. Studies by Bovey and Kolthoff (65) havedemonstrated that the oxygen inhibition period observed for emulsion polymerisation is proportional to the amount of oxygen present.

With a small amount of A.B.I.N. as initiator, to generate free radicals, in the same styrene - soap solution a curve was obtained after irradiation which showed a slight overall increase in Λ without the original arrest (graph 3). The vast increase in Λ in dilute solutions, due to hydrolysis,

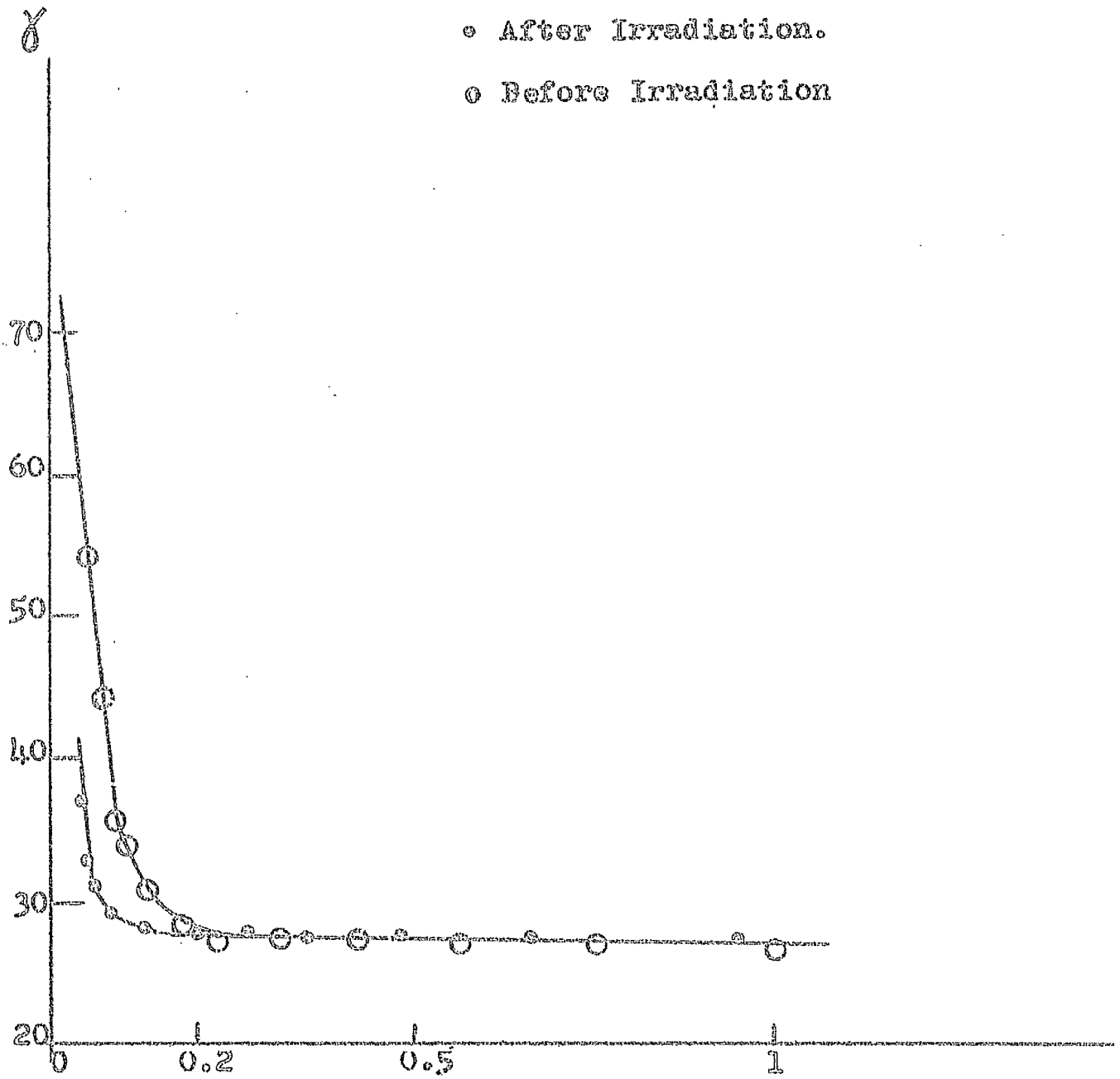

SODIUM OLEATE + STYRENE
Λ
x Before Irradiation.
o After Irradiation.
100
90
80
70
60
50
40
30
20
0
0.5
1.0
1.5
(√C x 10)

GRAPH 3

is still evident but the absence of the break point means that a certain amount of polymerisation has been encouraged.

The results of measurements on the Sugden surface tension apparatus on the same solutions are presented in graph 4 as plots of γ versus concentration in weight per cent. After being subjected to irradiation the solution gives rise to a curve displaced from that before irradiation, decreasing supposedly from the water value of 72 dynes/cm^2 to a constant value of 27 dynes/cm^2. The calculated values are not sufficient however to say whether the difference between the two solutions is due to complete polymerisation or whether it is simply due to a shift in C.M.C. caused by partial polymerisation. The C.M.C. as depicted by this method occurs about 0.11%, which is slightly higher than indicated by conductivity. It would be wrong to say that in this case it had been eliminated by the formation of polymicelles since there is a distinct change in slope as with the unirradiated solution. It is worth noting however that

SODIUM OLEATE



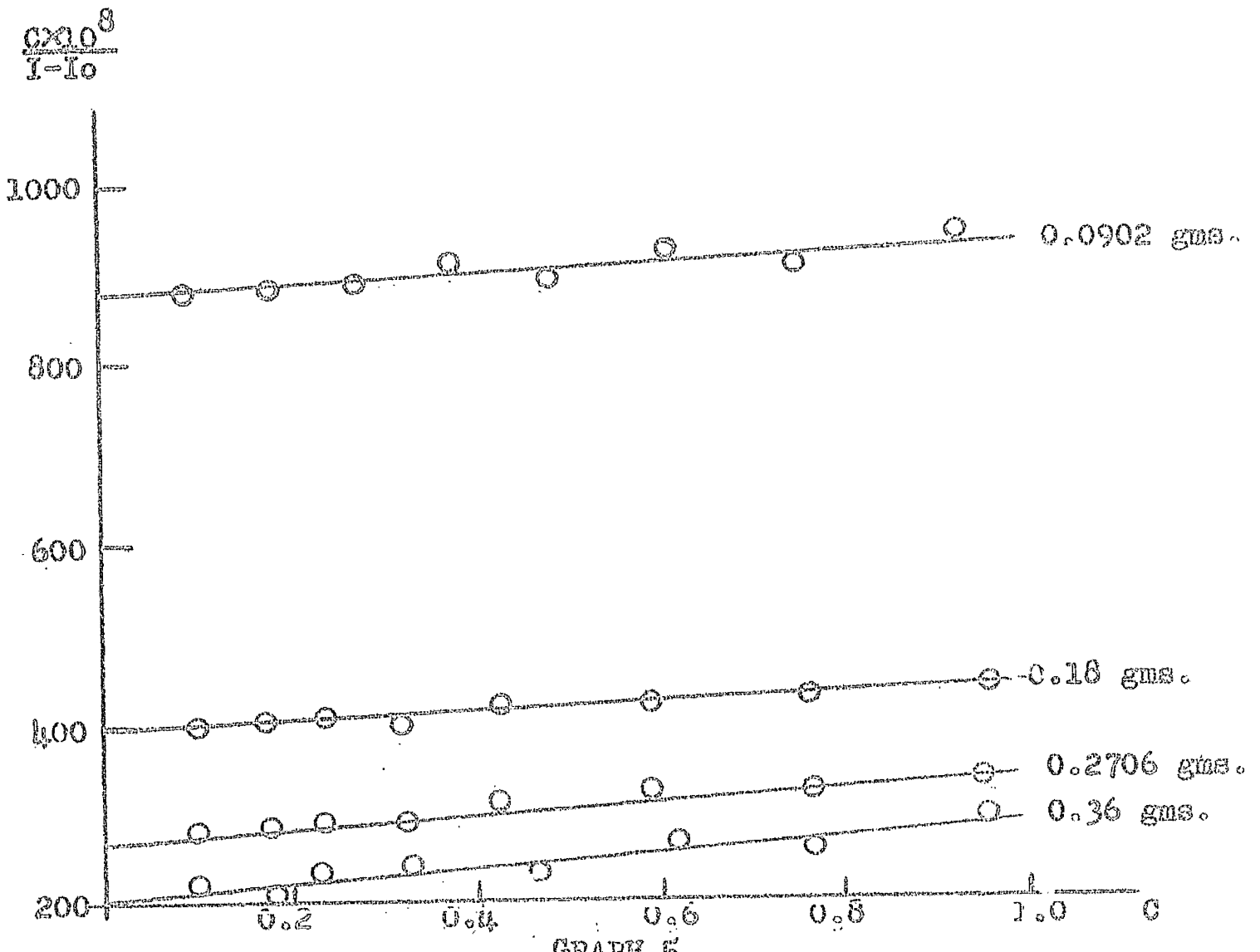
GRAPH 4

interfacial measurements do not give a true indication of bulk properties of a solution as opposed to conductivity measurements.

Acidification, after irradiation, of four solutions of 3% sodium oleate containing different amounts of styrene (solubilised by shaking at 30°C for 24hrs), gave rise to four fractions of polymer. The molecular weights of these fractions were then determined by light scattering using methyl ethyl ketone as solvent. P(θ), the dissymmetry factor, was found to be very close to unity for all four samples so that the molecular weights could be evaluated directly from the intercept of the $\frac{C}{I}$ versus C curves (graph 5), by the method of Debye (eq. 23). Final analysis on the four fractions are tabulated below in table I. The amounts of styrene are added to 50 c.c.s. of a 3% sodium oleate solution.

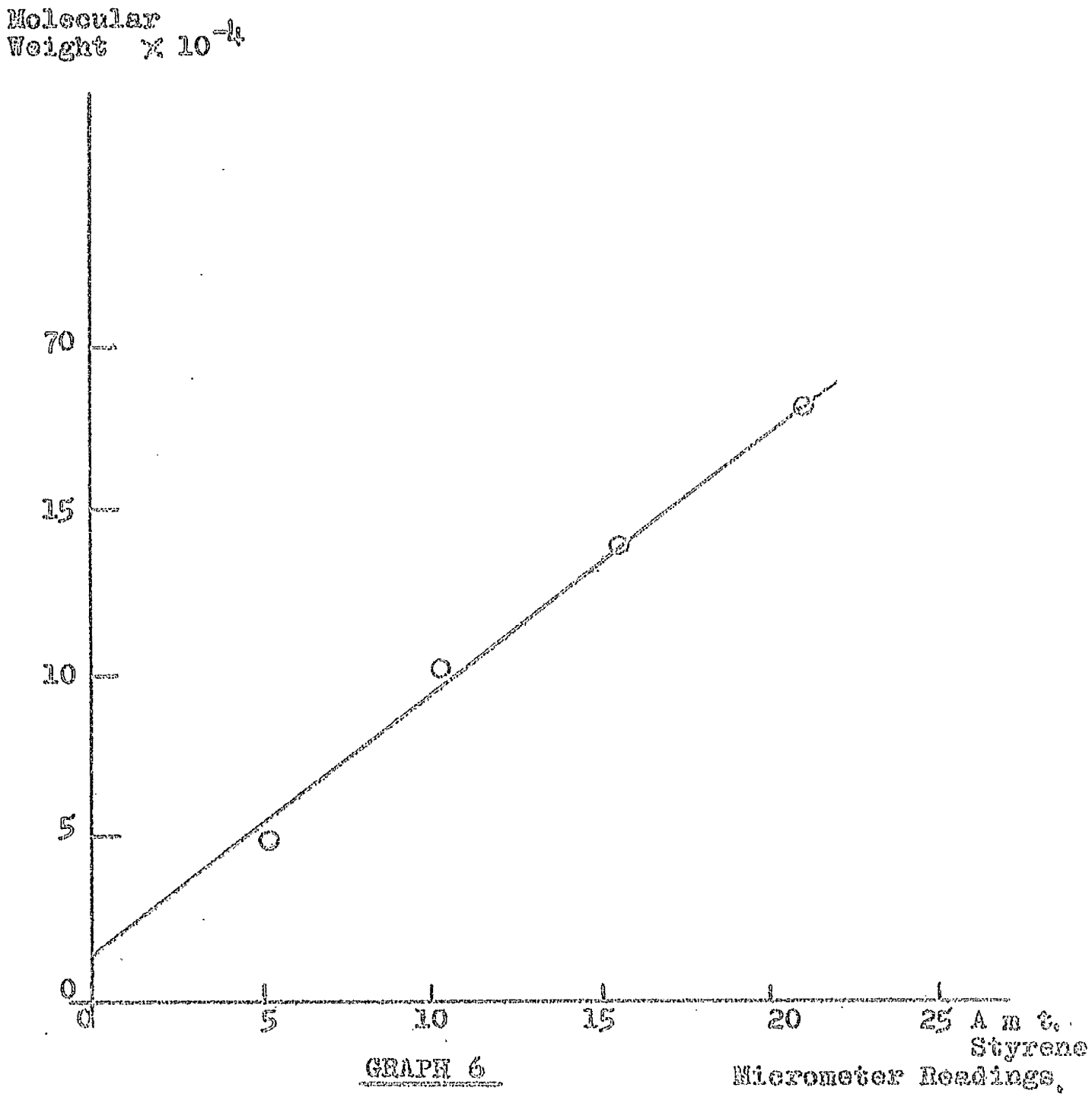
SODIUM OLEATE + STYRENE

STYRENE WTS/50 c.c.s. 3% Soap.



GRAPH 5.

SODIUM OLEATE + STYRENE.



GRAPH 6

Table I.

Wt. Styrene in gms.	Extrapolated $\frac{C}{I}$	$\left(\frac{dn}{dc}\right)^2$	Mol. Weight.
0.3600 gms.	2.02×10^{-6}	0.0543	180,000
0.2704 gms.	2.64×10^{-6}	0.0536	137,700
0.180 gms.	3.96×10^{-6}	0.0493	101,000
0.0902 gms.	8.74×10^{-6}	0.0486	46,400

The molecular weights for the four fractions, plotted as a function of the weight of styrene added, gave almost linear dependence which when extrapolated to zero styrene content gave approximately 13,000 for the micellar weight of the initial soup. Extrapolation was very hazardous, 13,000 being the mean of a range of possible values. Dividing by 304, the molecular weight of sodium oleate, indicates an apparent association number of 45 molecules per micelle.

The apparent molecular weights of the polymers, especially in the regions of high styrene content, are much higher than could be accounted for by a linkage of styrene and soap

molecules within single micelles. It is worth noting that after irradiation the solutions developed little or no turbidity such as might be expected to result from the formation of insoluble polystyrene. Also that the yields obtained were extremely low but still greater than the amount of styrene present e.g.058 grams polymer from 0.270gms. styrene and 1.5 gms. sodium oleate.

Mechanism of the Polymerisation:-

The styrene monomer when shaken up with the sodium oleate solution will distribute itself between the interior of the micelles and the water. Polym erisation is initiated by the reaction of a free radical, generated from A.B.I.N. by U.V. light, with a monomer molecule. Since A.B.I.N. is more soluble in oil than water the initiating free radicals will come into contact with solubilized styrene in the micelle interior. The polymerisation reaction can proceed rapidly in the micelles because of the relatively high concentration of solubilized monomer which is available to the free radicals.

[Polymethyl methacrylate polymerised by A.B.I.N. and labled with radioactive C^{14} has been shown to contain radical fragments $(CH_3)_2-\overset{CN}{C}-$ in the ratio of two per molecule(66). This suggests that coupling is the dominant chain terminating process in this case and that disproportionation occurs at most to a minor extent only. Detailed analysis of kinetic data on the rate and degree of polymerisation, although possibly more susceptible to errors of interpretation, leads to the same conclusion (67,68,69). It cannot be assumed however that the same chain terminating process will be invoked with the oleate-styrene copolymers.]

The process, up to this point, is similar to emulsion polymerisation whose mechanism was elucidated largely by Harkins and co-workers(70). They proved that polymerisation occurs in the micelle and that the styrene content of the micelle is augmented by diffusion of single styrene molecules from the styrene emulsion droplets via the aqueous phase. The droplets are considered to act merely as reservoirs of styrene. Eventually the small polymer formed in the micelle interior becomes too large and emerges from the

micelle but it retains soap molecules adsorbed on its surface.

In the case in question there is no such styrene reservoir but there is the possibility that the unsaturated soap molecules can enter into the polymerisation mechanism . Judging by the high molecular weights obtained it seems probable that, instead of the micelles retaining their character by simple linkage of the C=C double bonds, there has been a spliting of the micelles along with the polymerisation to form what could be termed a polysoap (fig.3). On a weight comparison basis between styrene added and yield obtained these polysoaps would contain 3 soap like side chains to 8 styrene groups, as shown. On this basis the polymer of molecular weight 180,000 would contain 90 such units which after termination could have adopted a micellar like configuration with the ionic groups at the surface and the interior jumbled up as a random coil. If the above speculations are correct then some of the sodium oleate micelles will become a styrene-oleate polymer surrounded by the excess soap in the form of reconstituted micelles. If there are sufficient polysoap molecules present

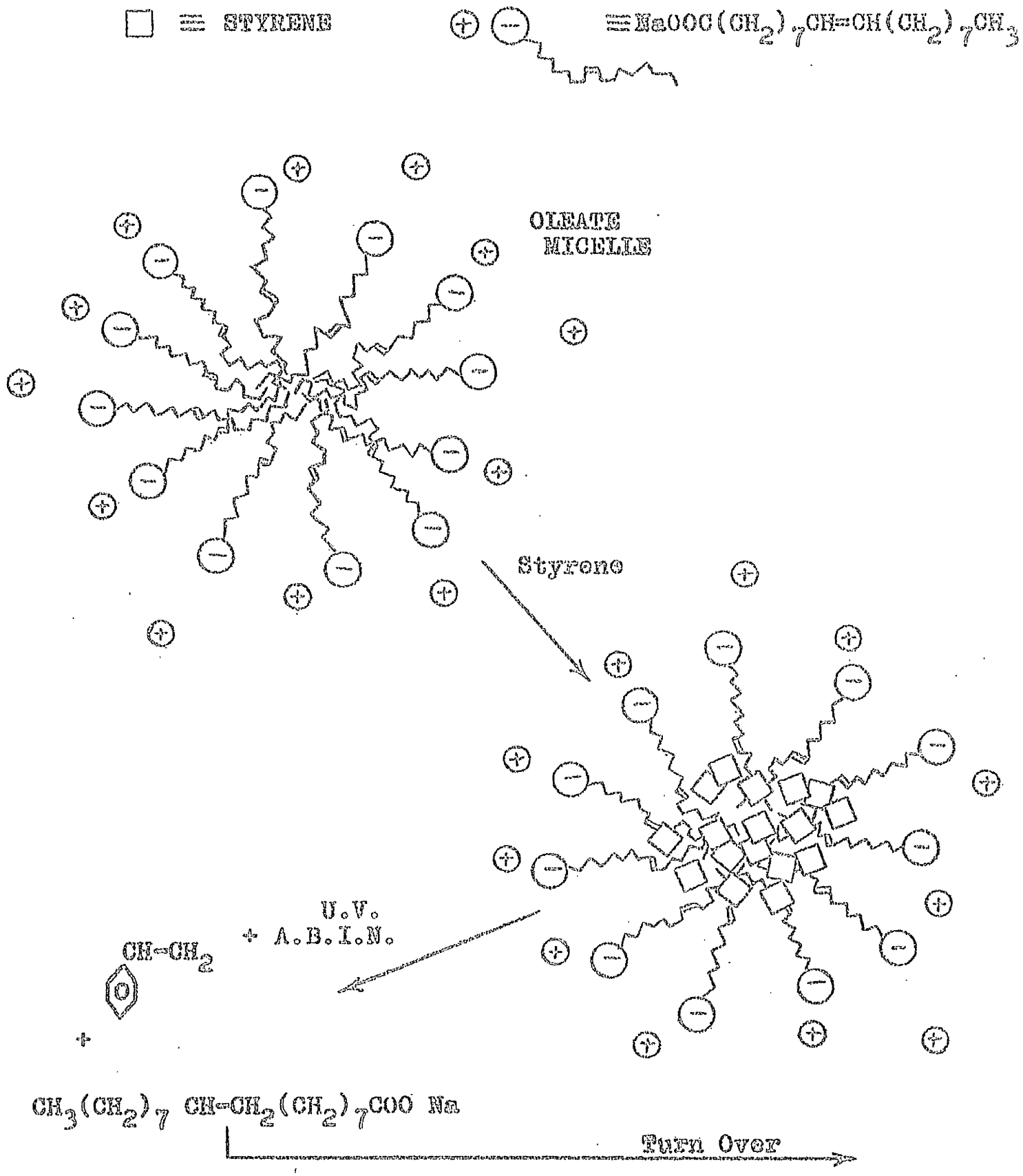
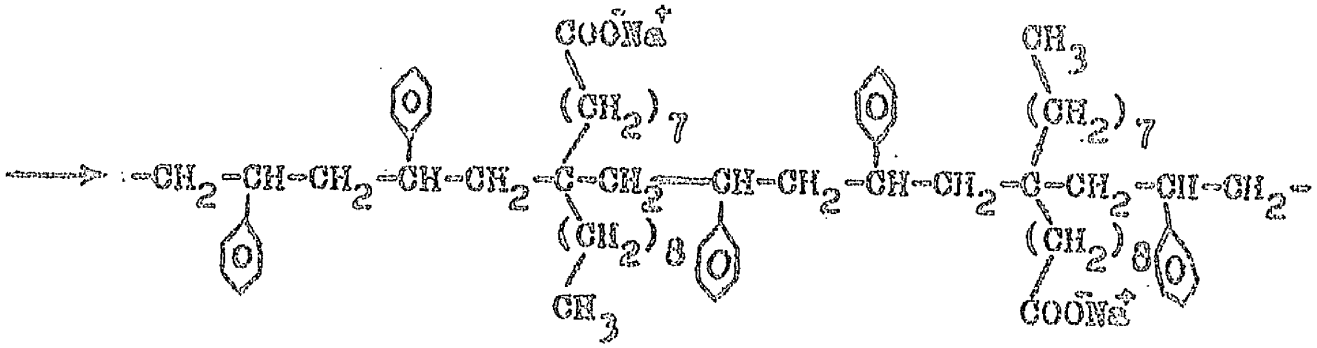
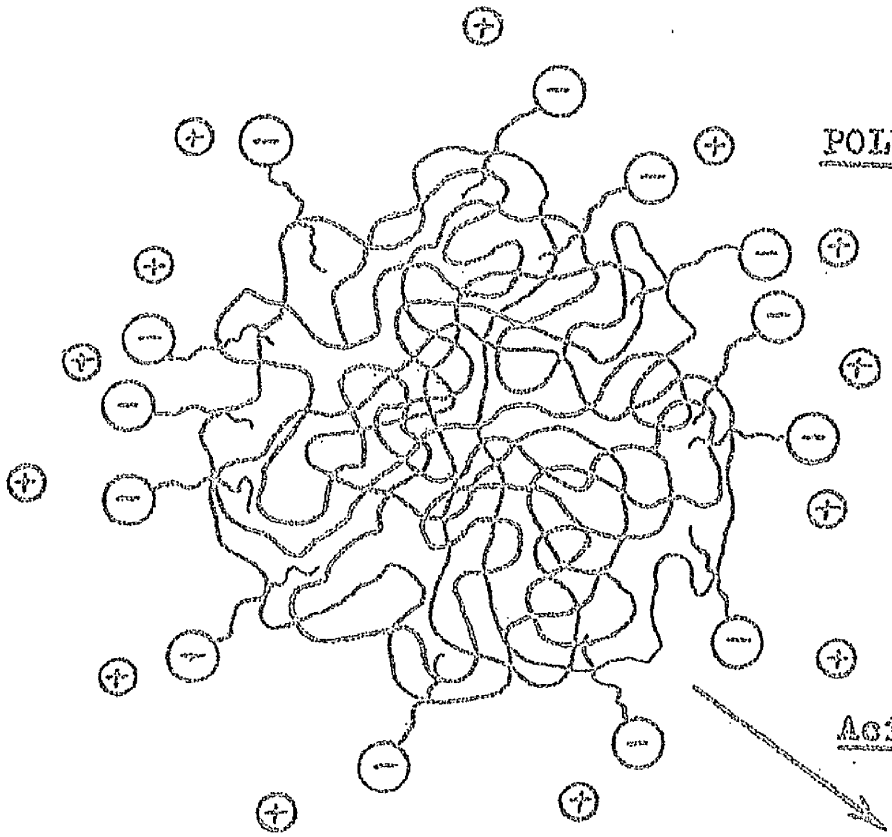

□ ≡ STYRENE
≡NaOOC(CH2)7CH=CH(CH2)7CH3
OLEATE MICELLE
Styrene
U.V.
+ A.B.I.N.
CH-CH2
O
CH3(CH2)7 CH-CH2(CH2)7COO Na
Turn Over

FIG 3.





POLYMER

the solution would exhibit no C.M.C. as observed. The molecular weight of the polysoaps may be expected to drop as the styrene content is reduced but it would be incorrect to attach any significance to the extrapolated value of 13,000 as the micellar weight of sodium oleate. What was thought to be initially the association number of 45 is more likely to be the number of sodium oleate molecules capable of entering into the mechanism by this method of polymerisation. Indeed if one considers polysoap (1) containing 8 styrene molecules to 3 oleate with a molecular weight of 180,000, then this polyelectrolyte would contain 40 oleate molecules. This is close to the extrapolated value.

A similar set of runs using divinyl benzene in place of styrene were unfortunately non productive. Even after 3/4 of the solubilization limit had been added, plus initiator, followed by 20 hrs irradiation, only the starting material in the form of oleic acid could be extracted.

As anticipated conventional light scattering technique cannot be applied to sodium oleate solutions. The light scattered by such solutions is vast at low concentrationsdue

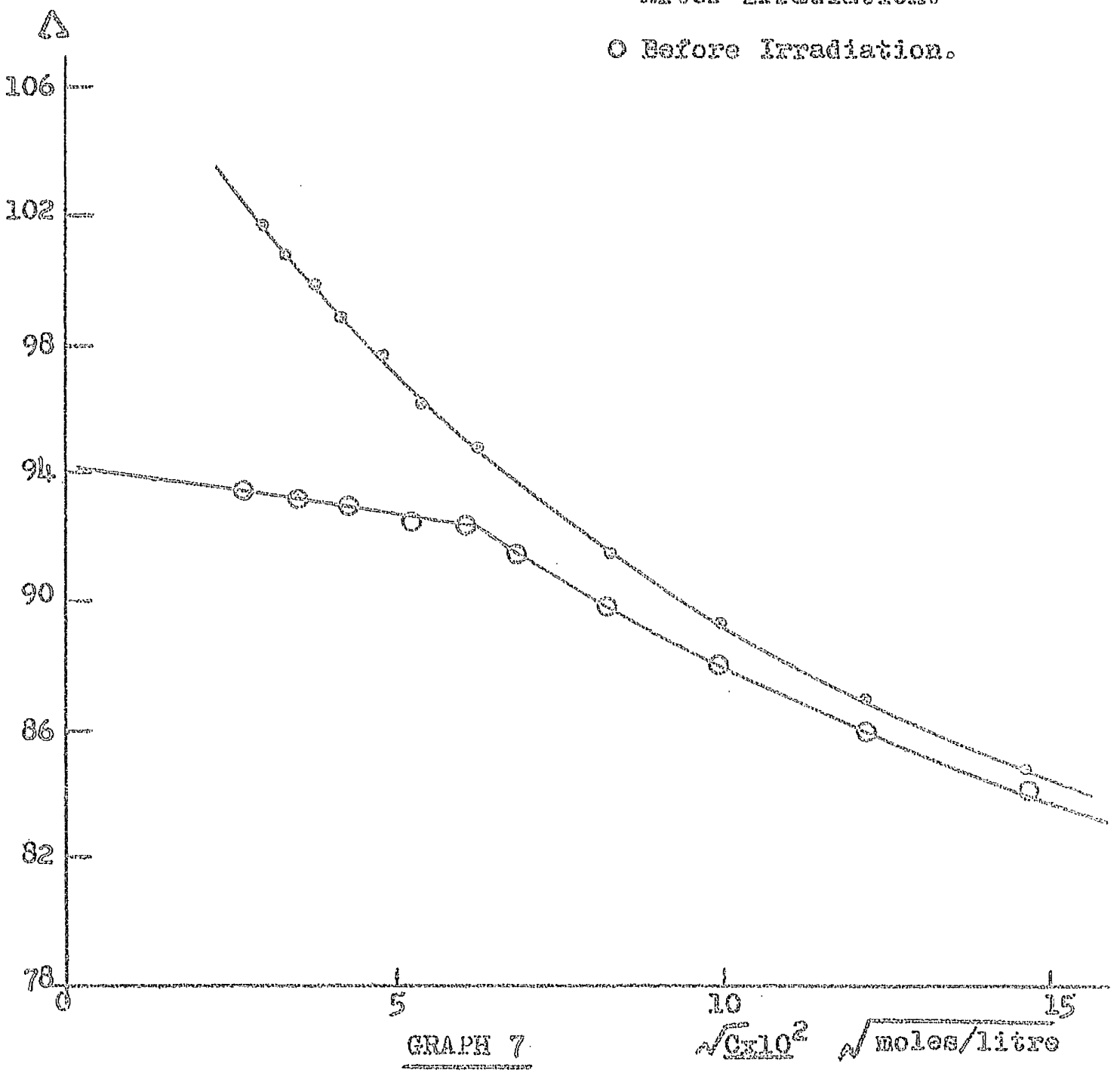
to the fatty acid molecules formed by hydrolysis being immiscible with water. An attempt was made to counteract the hydrolysis by added NaOH but while this measure reduced the light scattered by the solutions at low concentrations it had a marked effect on the intensity at higher concentrations, presumably due to an alteration in the size of the micelles.

Sodium Undecenyl Sulphate.

In order to try and form a polymicellar solution without the added complications of a solubilized hydrocarbon in the micelles experiments were carried out on the unsaturated anionic detergent sodium undecenyl sulphate (S.U.S.). The chance of radical formation may be enhanced with this molecule since the C=C double bond is situated at the end of the paraffin tail.

Except for the addition of styrene the technique adopted for encouraging polymerisation in the S.U.S. solutions was exactly the same as that for sodium oleate. Graph (7) illustrates the relationship between the equivalent conductivity Λ and $\sqrt{C}$ in $\sqrt{}$ moles/litre for a solution of S.U.S. before and after irradiation. The deviation of slope with

SODIUM UNDECENYL SULPHATE



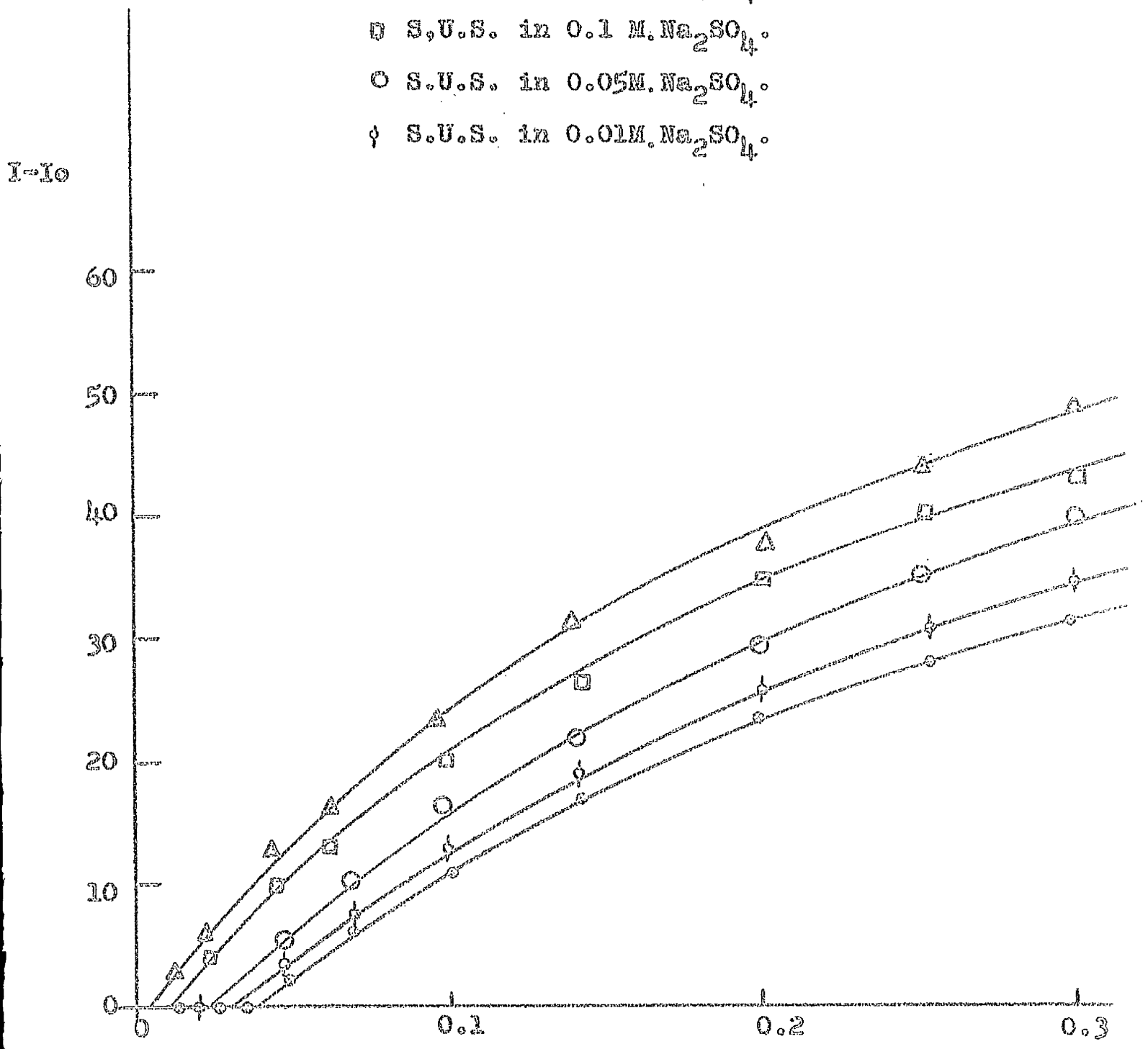
GRAPH 7

the solution before irradiation is due to dissociation of the micelles into single ions at the C.M.C.. This is not apparent after irradiation, as the curve continues to rise quite steeply below the C.M.C.. The lack of dissociation can be accounted for by a stabilization of the micelles by polymerisation. The polymicellar solution has a higher conductivity than the same number of single ions in solution .

Results of light scattering in solutions of S.U.S., with and without added salt, before irradiation, are presented in graphs (8) and (9). In the first of these graphs the reduced intensity I-Io is plotted as a function of the concentration of soap in wt. per cent. The unassociated soap is seen to scatter the same amount of light as the solvent up to the critical concentration thereafter increasing steadily throughout the concentration range measured. In each solvent the C.M.C. of the detergent was obtained by extrapolating intensity data, obtained above the C.M.C., back to the value of the solvent. Each of the micellar weights was evaluated by the method of Debye(eq. 23) using the intercept values $\frac{(C-C.M.C.)}{I-Io}$ at zero (C-C.M.C.) from graph (9) and refractive index increments obtained from the

SODIUM UNDECENYL SULPHATE

- ○ S.U.S. in water.
- △ S.U.S. in 0.2 M. Na_2SO_4.
- □ S.U.S. in 0.1 M. Na_2SO_4.
- ○ S.U.S. in 0.05M. Na_2SO_4.
- ◊ S.U.S. in 0.01M. Na_2SO_4.

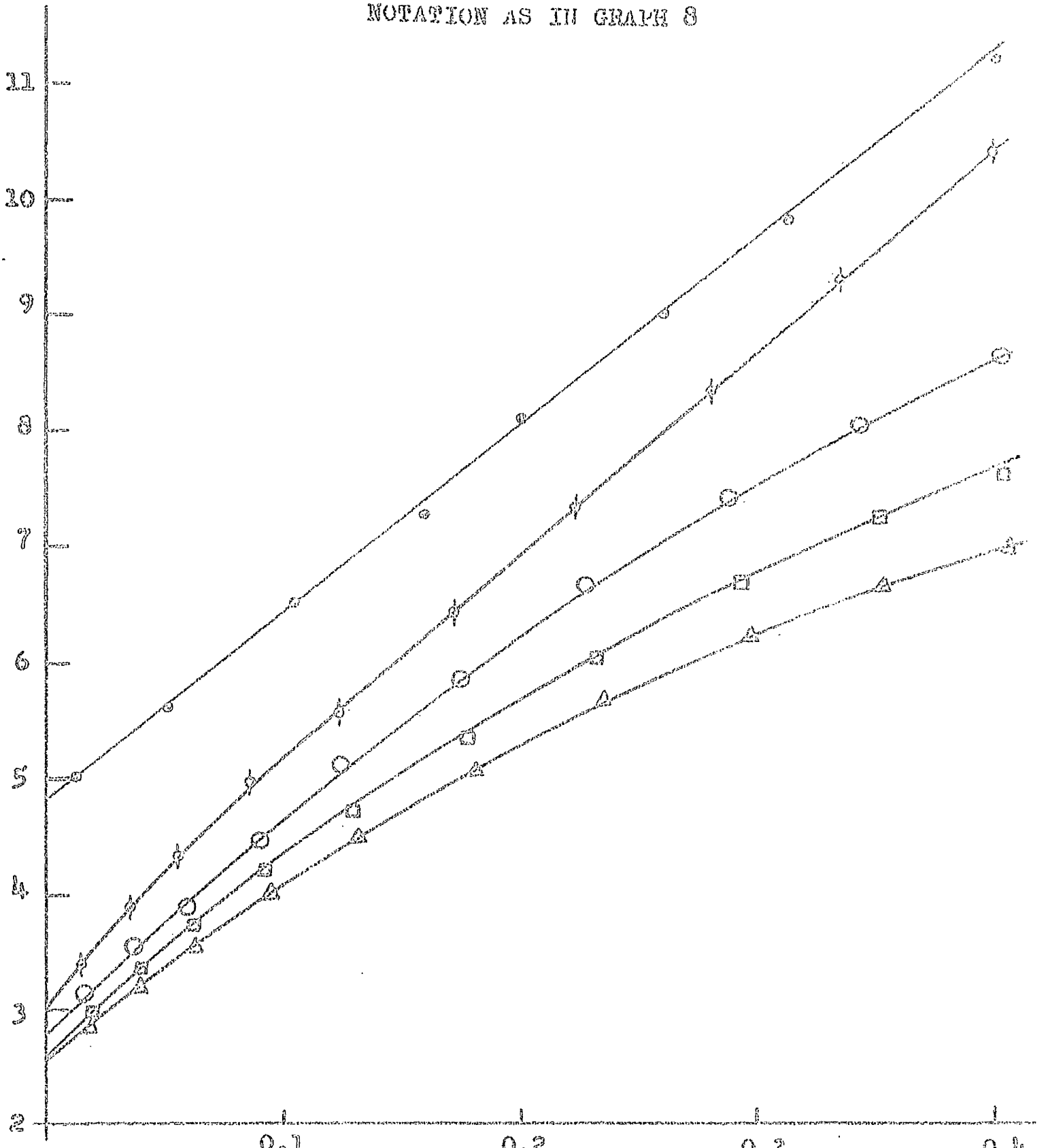


GRAPH 8

C.M.C. x 10^3
I-Io

SODIUM UNDECENYL SULPHATE.

NOTATION AS IN GRAPH 8



GRAPH 9

Rayleigh Interferometer. The simplified Debye approach was adopted, as the more refined theory of Prins presented earlier leads to a correction for charge effects which is rather small and in the region of the experimental error e.g. for $C_{12}H_{25}OSO_3Na$ the micellar weight changes from 24,200 to 26,700 using this theory. It must be remembered also that the values of p and n are obtained from the second virial coefficient which in turn is calculated from the slope of the $\frac{(C-C_1)C}{I-I_0}$ V's (C-C.M.C.) curve. This is where the greatest error lies owing to uncertainties in the correct value of the C.M.C. and the very low intensities involved. Once electrolyte is added to the system the correction factor becomes negligible e.g. for $C_{12}H_{25}OSO_3Na$ in 0.02 M NaCl, the micellar weight alters from 27,600 to 28,800 according to Prins' treatment.

The dependence of the micelle weight on the concentration of sodium sulphate is given in Table 2.

TABLE 2.

Conc. Na_2SO_4 (Molar)	Lim: $\frac{C-Co}{I-Io}$	$\left(\frac{dn}{dc}\right)$ const. elect. conc.	Micellar Weight M.
0	4.9×10^{-3}	0.120	30,800
.01M	3.01×10^{-3}	0.116	48,800
.05M	2.8×10^{-3}	0.117	51,200
0.1M	2.7×10^{-3}	0.119	52,000
0.2M	2.62×10^{-3}	0.118	54,100

In agreement with other light scattering studies on detergents the data presented here indicate an increase in the apparent micelle weight with an increase in the concentration of simple electrolyte. The presence of electrolyte also leads to a lowering of the C.M.C. of the detergent solution. In water a micellar weight of 30,800 is obtained corresponding to an association number of 120. The calculated micellar weight increases rapidly with small additions of Na_2SO_4 and appears to be nearly independent of

electrolyte concentration above 0.05M having a value of about 53,000.

It was found that after irradiation of solutions of S.U.S. with and without added electrolyte, measurements could be made below the C.M.C., indicating the presence of micelles stabilized by polymerisation. Plots of the reduced intensity against concentration(graph 10) show a surprising reduction in the light scattered with increase in electrolyte content. As with the unirradiated soap $\left(\frac{dn}{dc}\right)_{\text{const.elect.conc.}}$ values appeared to be constant and along with the extrapolated $\frac{c}{I-Io}$ values (graph 11) led to apparent micellar weights which decreased with increasing electrolyte concentration.

It was realised that the polymicellar solutions afforded a means of determining the refractive index increments at constant chemical potential of electrolyte, $\left(\frac{dn}{dc}\right)_{\mu\ \text{electrolyte}}$. In ionic solutionsthis is, thermodynamically, the correct refractive index increment to use in the analysis of micellar weights by light scattering. This increment $\left(\frac{dn}{dc}\right)_{\mu}$ cannot be determined for ordinary micellar solutions as its calculation involves dialysing solutions against the appropriate concentration of salt before measurement and the micelles

SODIUM UNDECENYL SULPHATE.

O S.U.S. in water.

X S.U.S. after Polymerisation in water.

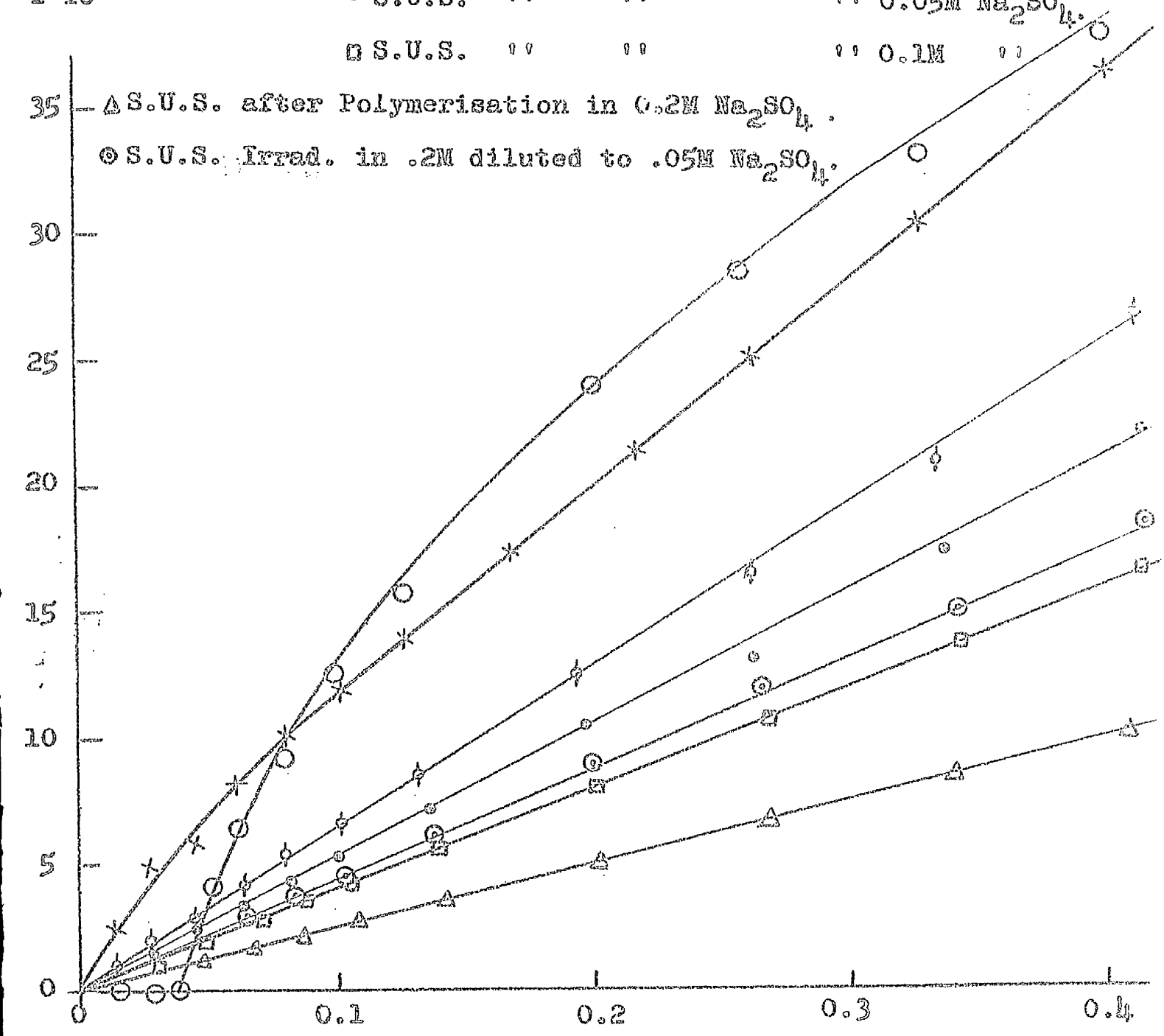
ϕ S.U.S. " " " 0.01M Na_2SO_4.

∘ S.U.S. " " " 0.05M Na_2SO_4.

□ S.U.S. " " " 0.1M "

△ S.U.S. after Polymerisation in 0.2M Na_2SO_4.

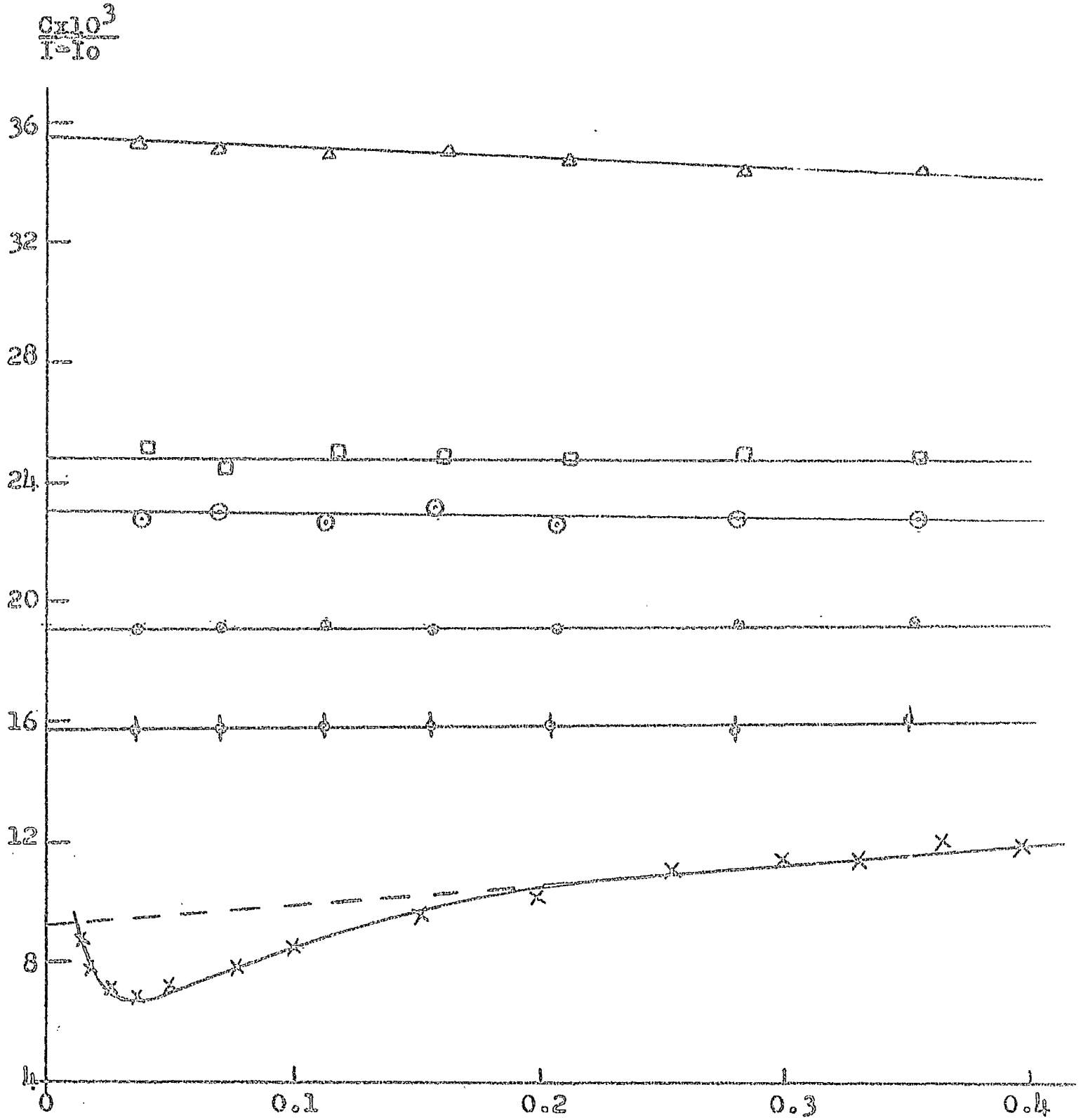
⊙ S.U.S. Irrad. in .2M diluted to .05M Na_2SO_4.



Graph 10

SODIUM UNDECENYL SULPHATE.

NOTATION AS IN GRAPH 10



GRAPH 11.

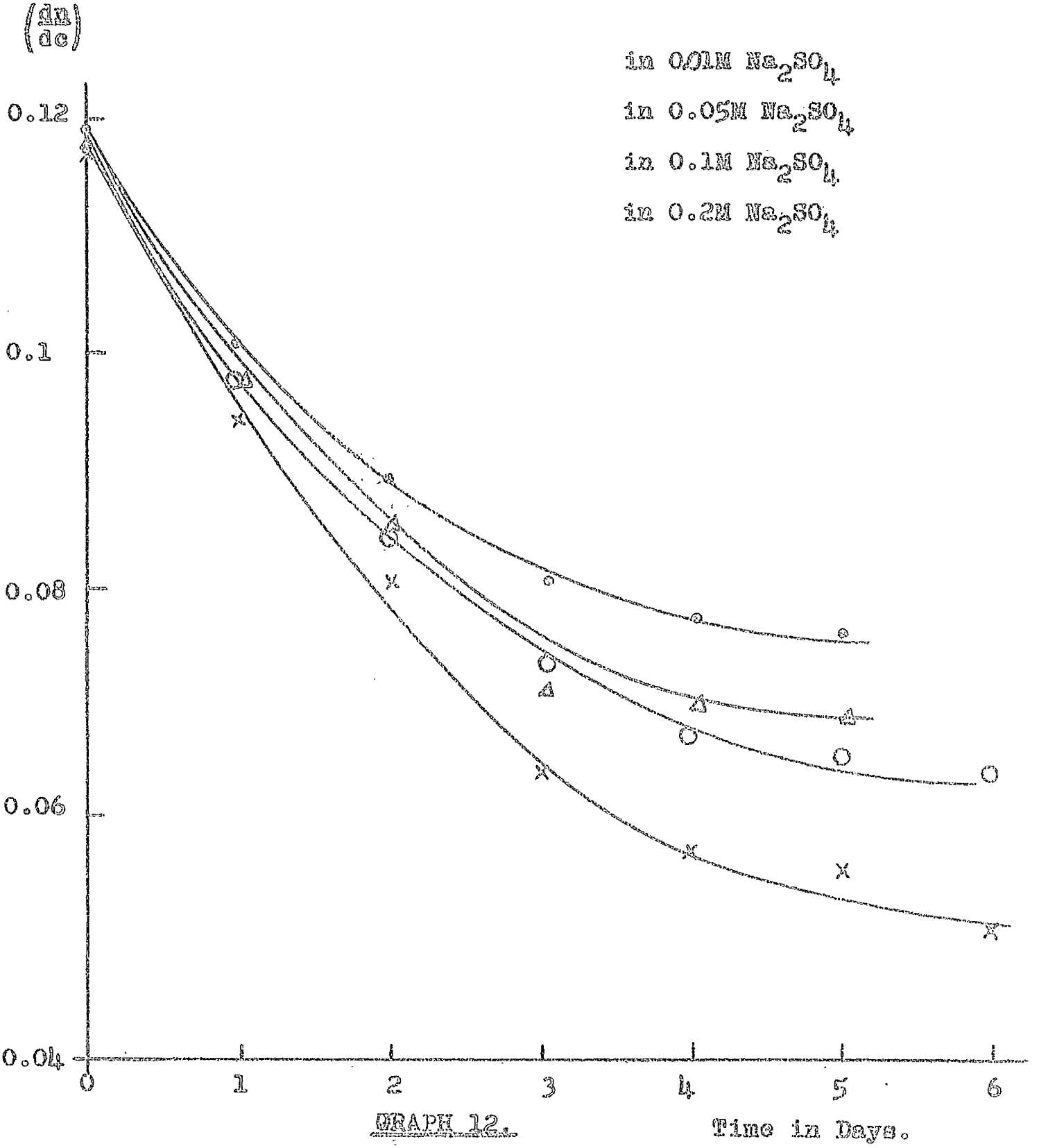
would simply dissociate and diffuse through the membrane as the monomeric ion content is reduced.

Dialysis Measurements:-

Samples of the polymicellar solutions were transferred to a piece of Visking tubing closed at one end. The tubing had previously been washed in distilled water to remove any soluble impurities. The open end was sealed simply by knotting and the dialysis bag so formed immersed in a solution of Na_2SO_4 of the same concentration. The external solution was changed daily for 5 days and a small amount of the dialysing solution withdrawn for $\left(\frac{dn}{dc}\right)$ estimation every 24hrs. Graph (12) illustrates the steady decrease in $\left(\frac{dn}{dc}\right)$ with time until a constant value is obtained. These estimations of $\left(\frac{dn}{dc}\right)_{\mu}$ electrolyte will be subject to considerable error as it was assumed in their calculation that the soap concentration in the dialysed solutions remained constant. However any unpolymerised soap will be included in the diffusible components. It was found that dialysis of polymicellar solutions in water and in 0.2M salt resulted

SODIUM UNDECENYL SULPHATE.

DIALYSIS EXPERIMENT.



GRAPH 12.

*

Note on Refractive Index Increments at Constant Chemical Potential of Electrolyte.

When a molecule in solution is surrounded by a binary system, selective adsorption of one of the components may occur. This is true when both components in the solvent are liquid or when one is a simple electroltye. The adsorption will alter the polarisability of the molecule thus affecting the intensity of the scattered light. It has been shown (110) that correct results may be obtained by measuring the refractive index increment at constant chemical potential of simple electrolyte.

If components 1,2 and 3 refer to solvent, micelle and simple electrolyte respectively then :-

$$\left(\frac{\partial n}{\partial c_2}\right)_{\mu_3} = \left(\frac{\partial n}{\partial c_2}\right)_{c_3} + \left(\frac{\partial n}{\partial c_3}\right)\left(\frac{\partial c_3}{\partial c_2}\right)_{\mu_3}$$

$\left(\frac{\partial n}{\partial c_2}\right)_{\mu_3}$ can be determined directly using a polymicellar solution which has been dialized against the same concentration of simple electrolyte.

in a loss of 20% of soap (by evaporation and weighing). Applying this correction for ΔC gave $\left(\frac{dn}{dc}\right)_\mu$ electrolyte. Using these values along with the appropriate $\frac{C}{I-Io}$ extrapolated leads to the results summarised in table 3.

TABLE 3.-

Salt Conc. Na_2SO_4	Lim. $\frac{C}{I-Io} \times 10^3$	$\left(\frac{dn}{dc}\right)$ const. electrolyte. conc.	$\left(\frac{dn}{dc}\right)_\mu$	Polymicellar Weights.
0.01N	15.7	0.116	0.095	13,950
0.05M	19.0	0.118	0.0875	13,600
0.1M	24.7	0.119	0.080	12,500
0.2M	35.5	0.118	0.065	13,200

The value in water cannot be obtained because of uncertainties in the extrapolation. The results indicate that irrespective of salt content the micelles seem to form polymicelles of molecular weight about 13,500 there being 52 molecules per polymicelle. This can only be an accurate measure of the association number of the micelles if there is complete polymerisation within them and no coalescence between micelles

during polymerisation.

Further evidence for partial polymerisation was gathered by diluting down an S.U.S. solution in 0·2M Na_2SO_4 to 0.05M Na_2SO_4. This diluted solution was subjected to light scattering analysis using 0.05M Na_2SO_4 as solvent. As shown in graph 10 the resultant curve did not coincide with the original 0.05M Na_2SO_4 unirradiated proving that some polymerisation had taken place. Also it did not coincide with that for 0.2M Na_2SO_4 irradiated, after allowances had been made for the difference in $\left(\frac{dn}{dc}\right)_\mu$, indicating that there had been a change in dilution from 0.2M to 0.05M Na_2SO_4 supposedly connected with unpolymerised soap. There is the added possibility that some of the unpolymerised soap is absorbed in the polymicellar soap. In the calculation of $\left(\frac{dn}{dc}\right)_\mu$ the assumption has been made that unpolymerised ions are free to diffuse through the dialysis membrane.

Copolymerisation of solubilised styrene with S.U.S.

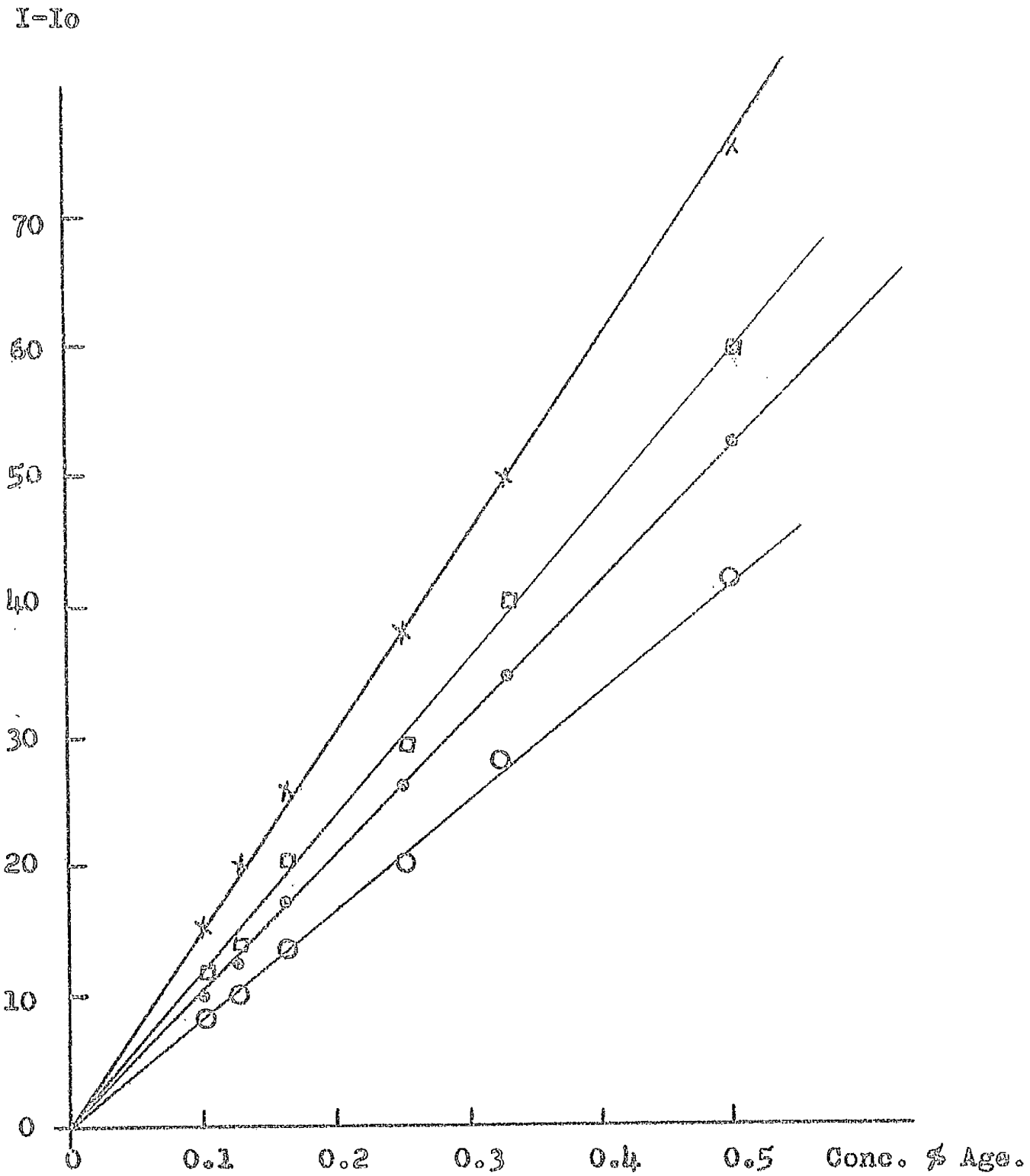
micelles using a similar procedure as with sodium oleate gave rise to a styrene S.U.S. polymicelle of molecular weight 18,700 at the highest styrnee content to about 14,900 at the lowest. The results are presented in graphs 13 and 14 and summarised in table 4.

TABLE 4:-

Amt. Styrene Gms. per. 150ccs. 1% S.U.S.	Lim. $\frac{C}{I-I_0} \times 10^3$	$\left(\frac{d\eta}{dc}\right)/c$	Polymicellar Weight.
0.153	6.45	0.128	18,700
0.1188	8.32	0.122	15,950
0.0845	9.7	0.118	14,650
0.051	11.9	0.119	14,900

Extrapolating back to zero styrene content from graph 15 yields a value of 13,000 for the initial micellar weight, assuming that polymerisation is confined to each micelle. Thus in the cases considered so far the extrapolated micellar weights are smaller (roughly 50% in this case) when taken from the data on polymicelles than from conventional methods.

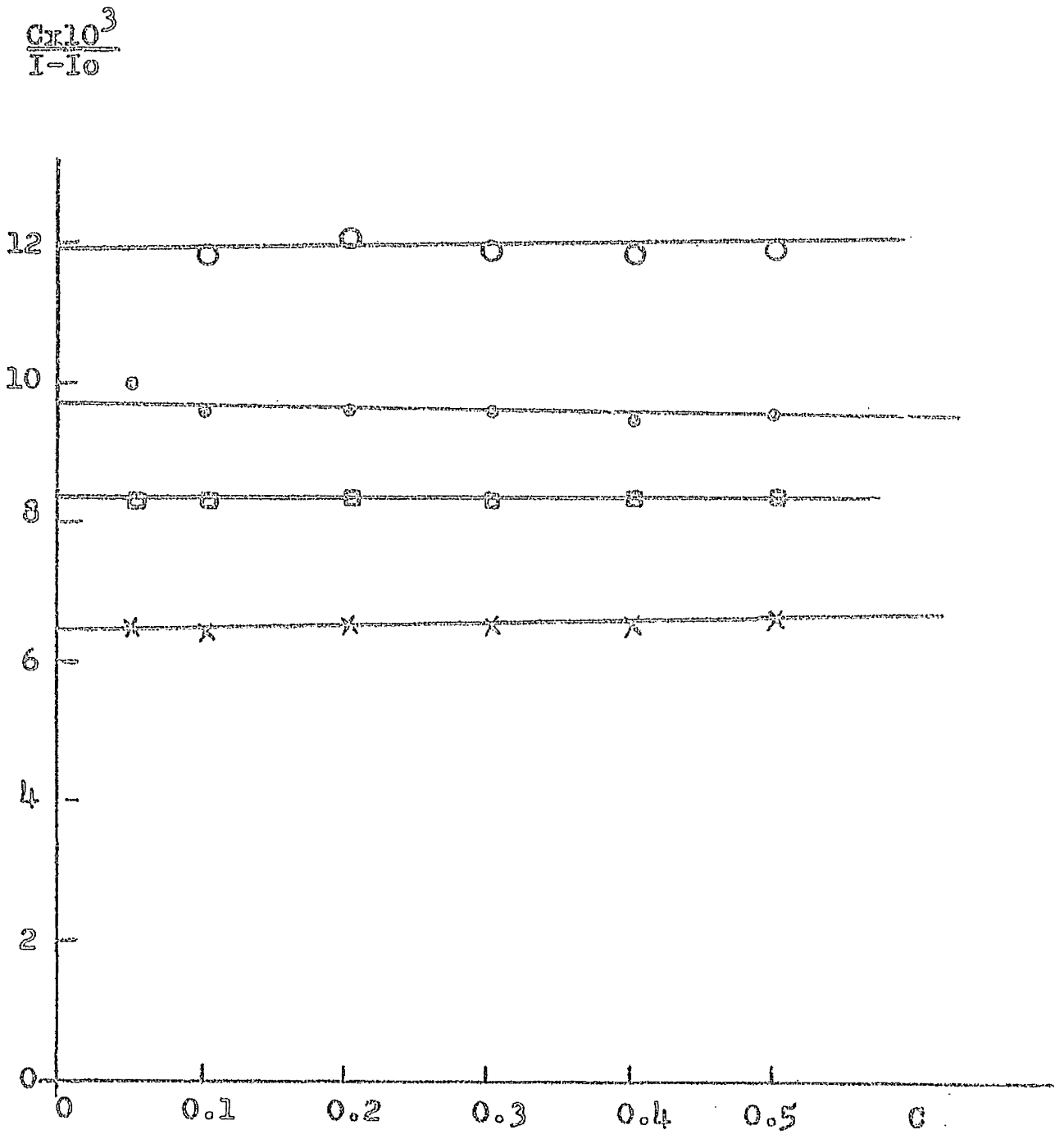
SODIUM UNDECENYL SULPHATE + STYRENE.



GRAPH 13

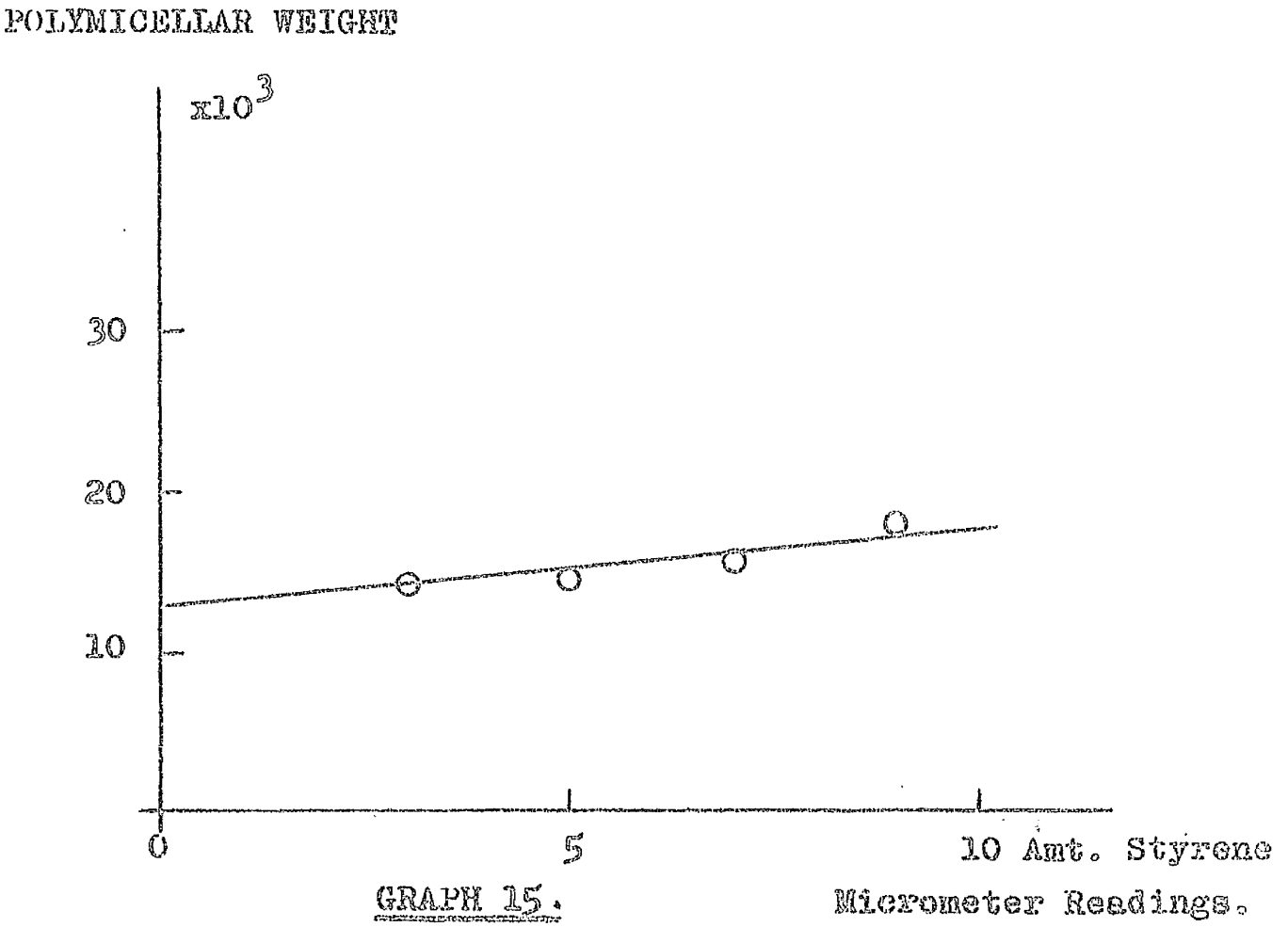
SODIUM UNDECENYL SULPHATE + STYRENE

NOTATION AS IN GRAPH 13



GRAPH 14

SODIUM UNDECENYL SULPHATE + STYRENE.



GRAPH 15.

This is to be expected with incomplete polymerisation where only part of the micelle is entering into the polymerisation.

Effect of Initiator:-

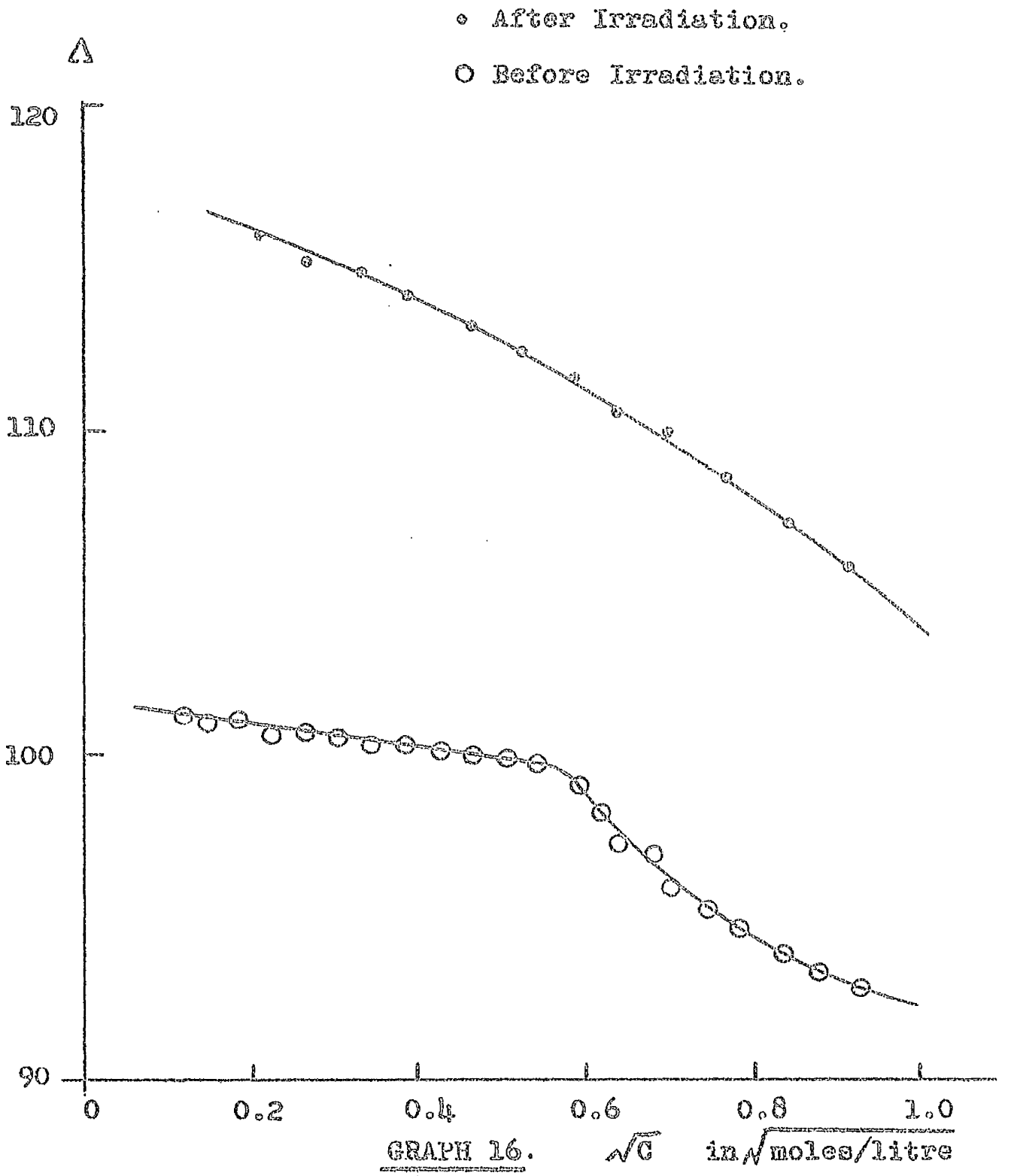
In order to check that the small additions of A.B.I.N. to the various sytems to promote free radical formation did not affect the light scattered by the polymicellar solutions a study was made on 0.01M Na_2SO_4 containing S.U.S. with varying amounts of A.B.I.N.. With additions of initiator up to 0.00195 gms. the I-Io versus C plots were superimposable. At much higher additions e.g. 0.0038 gms. A.B.I.N. the curve deviated slightly but since this was 10 to 15 times the amount used in the experiments it was concluded that any difference in weight incurred in introducing small quantities of A.B.I.N. (approx. 0.00025 gms.) had no adverse effect on the final result.

Undecenyl Trimethyl Ammonium Bromide :-

A similar series of experiments was conducted on the unsaturated cationic detergent undecenyl trimethyl ammonium bromide (U.T.A.B.). The plot of equivalent conductivity Λ at 25°C as a function of the square root of the concentration in moles/litre is shown in Graph 16. There is a distinct break in the curve for the unirradiated soap giving a value of 0.09% U.T.A.B. for the C.M.C.. The value obtained from light scattering (see graph 17) is 0.1%. The irradiated solution exhibits an overall increase in Λ of about 10% and, as in the other two cases, does not deviate in slope at the C.M.C. of the unirradiated solution.

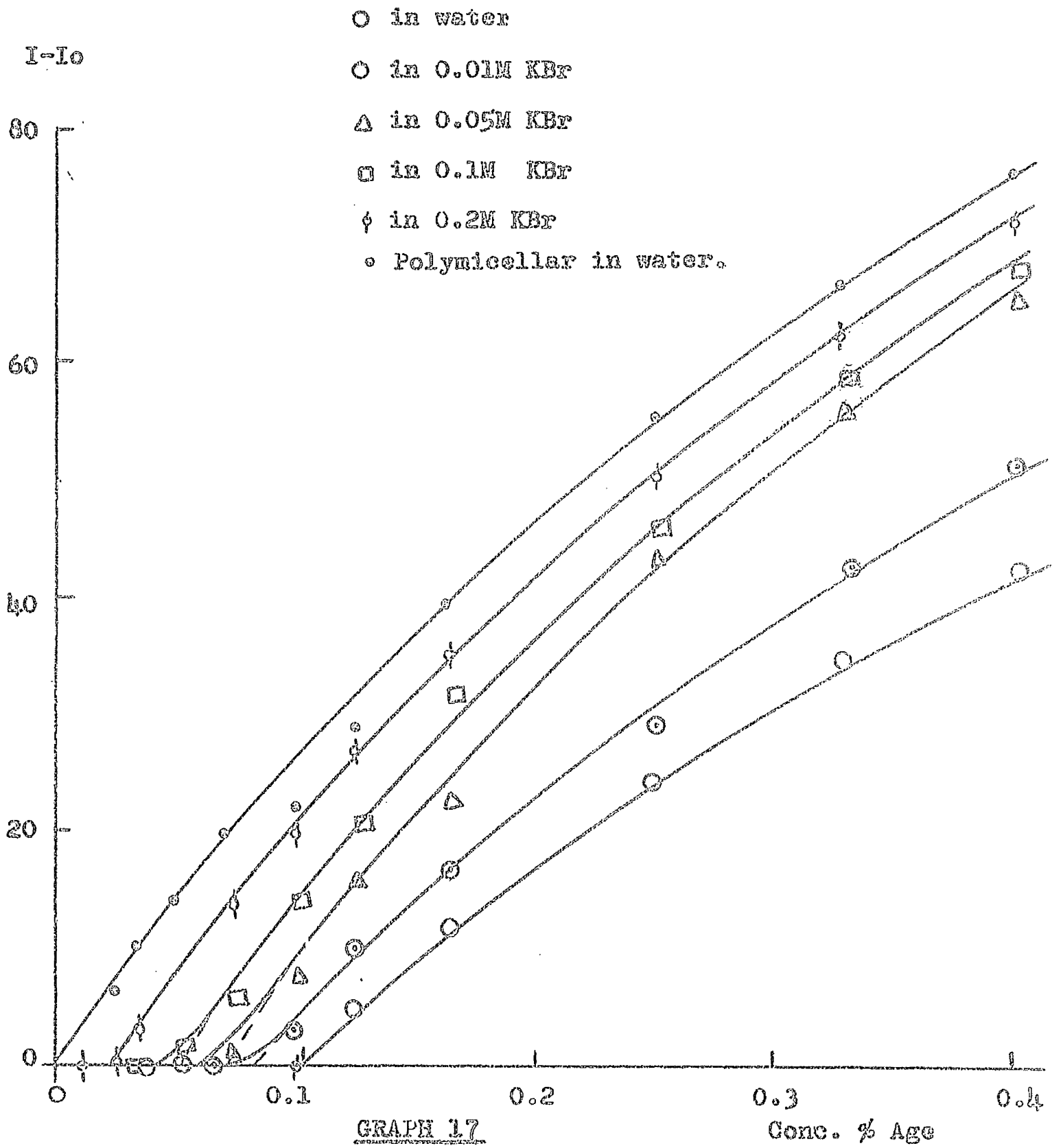
Results of light scattering in solutions of U.T.A.B. with and without KBr are presented in graphs 17 and 18. In each solvent the C.M.C. of the detergent was obtained by extrapolating intensity data back to the value of the solvent. It is precisely in this operation that the conventional process is vulnerable because of the extremely small intensities

UNDECENYL TRIMETHYL AMMONIUM BROMIDE



GRAPH 16.

UNDECENYL TRIMETHYL AMMONIUM BROMIDE

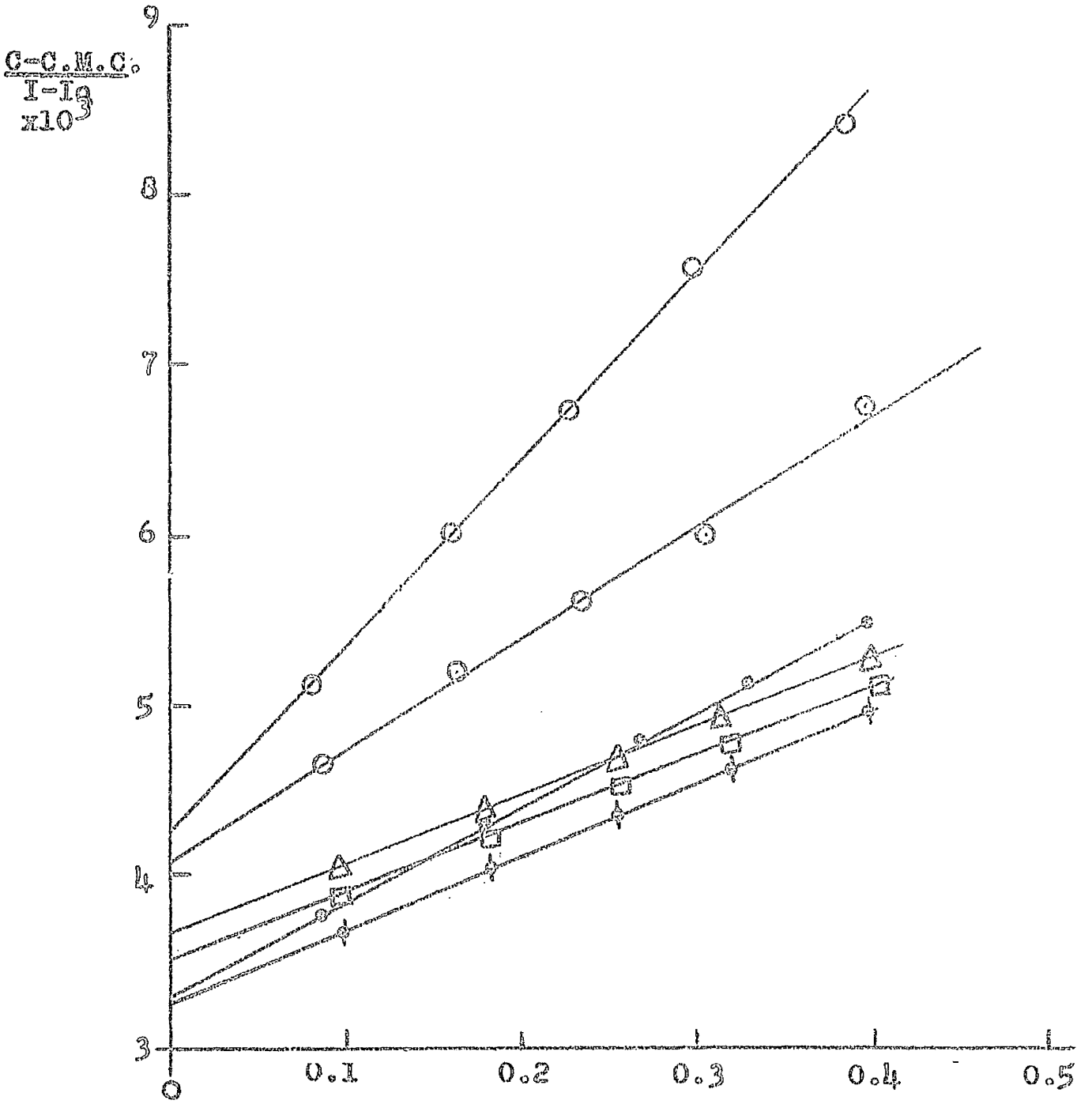


GRAPH 17

UNDECENYL TRIMETHYL AMMONIUM BROMIDE

IN KBr SOLUTIONS

NOTATION AS IN GRAPH 17



GRAPH 18

to be measured. However utilizing the most accurate C.M.C. values which could be obtained gave rise to a dependence of the apparent micellar weight M on the concentration of KBr as depicted in table 5.

TABLE 5.

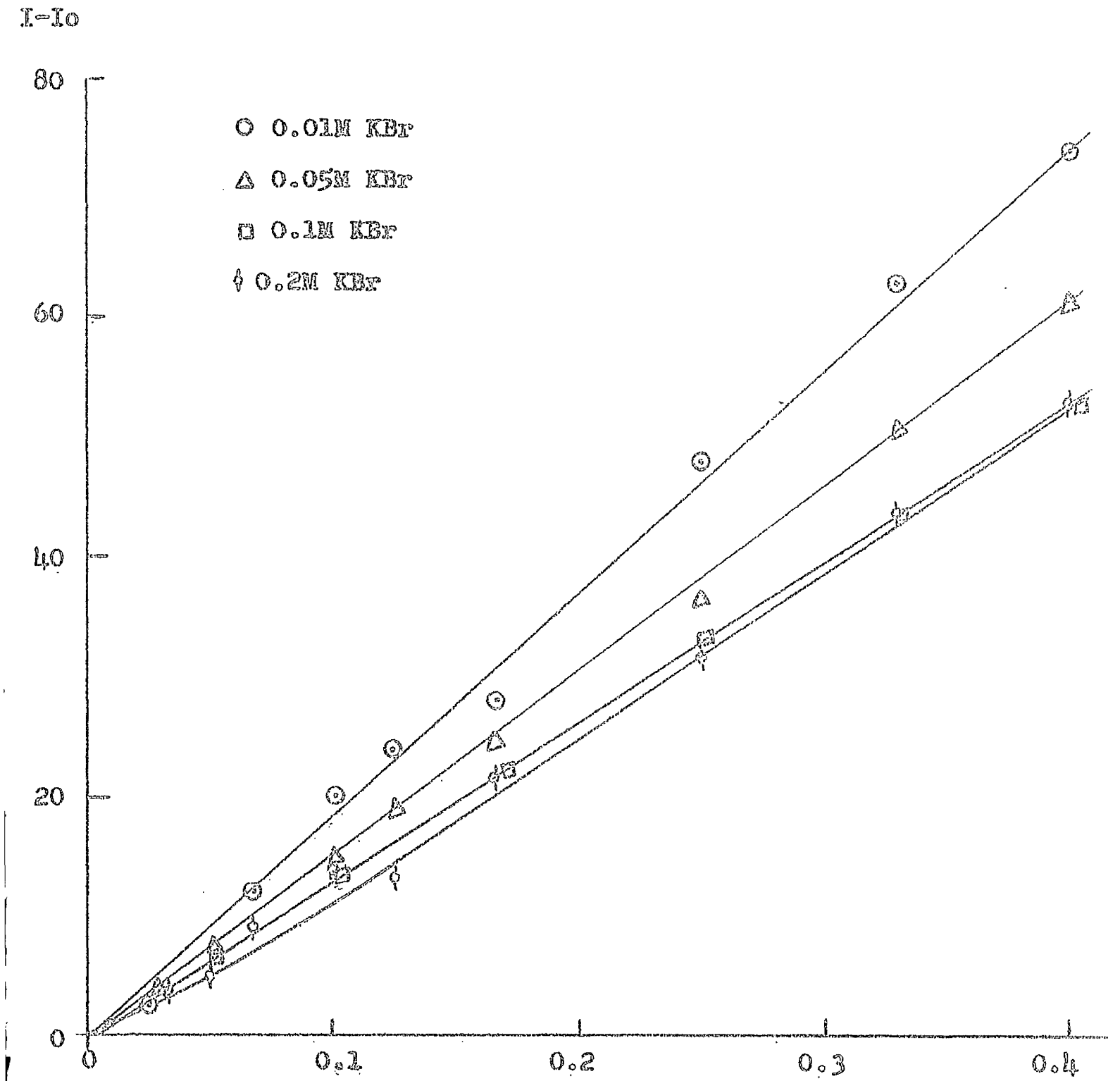
Conc.KBr. Molar	C.M.C. Co in %age By Wt.	$\text{Lim.}\frac{C-Co}{I-Io}\times10^{3}$	$\left(\frac{dn}{dc}\right)$ const. elect. conc.	M
0	0.105	4.25	0.167	13,300
0.01M	.085	4.08	0.162	18,400
0.05M	0.066	3.7	0.171	18,300
0.1M	0.047	3.5	0.172	19,000
0.2M	0.025	3.25	0.175	19,700

The $\left(\frac{dn}{dc}\right)$ measurements are made at constant concentration of electrolyte and can only be corrected to constant chemical potential by dialysis of the polymicellar solutions. Despite the limitations in the apparent micellar weights calculated in this instance, the normal effects of C.M.C. decreasing

and apparent weights increasing with increasing salt concentrations are evident.

As with S.U.S. it was possible to obtain measureable intensities on the polymerised soap at concentrations below the C.M.C. of the unpolymerised soap. The plots of I-Io versus C (graph 19) are almost linear but deviate slightly at lower concentrations, bending upwards at low electrolyte concentration and downwards at high (0.2MKBr). Contrary to expectation but in accordance with the S.U.S. findings the intercept on the $\frac{C}{I-Io}$ axis on graph 20 increases as the KBr concentration increases. The upward curvature at lower concentrations for the U.T.A.B. irradiated in 0.2MKBr indicates a decrease in molecular weight on dilution suggesting that the scattering unit is dissociating. It may be that at this relatively high concentration of electrolyte there is more unpolymerised material present as the $\frac{C}{I-Io}$ plots at lower concentrations of KBr do not exhibit this phenomenon.

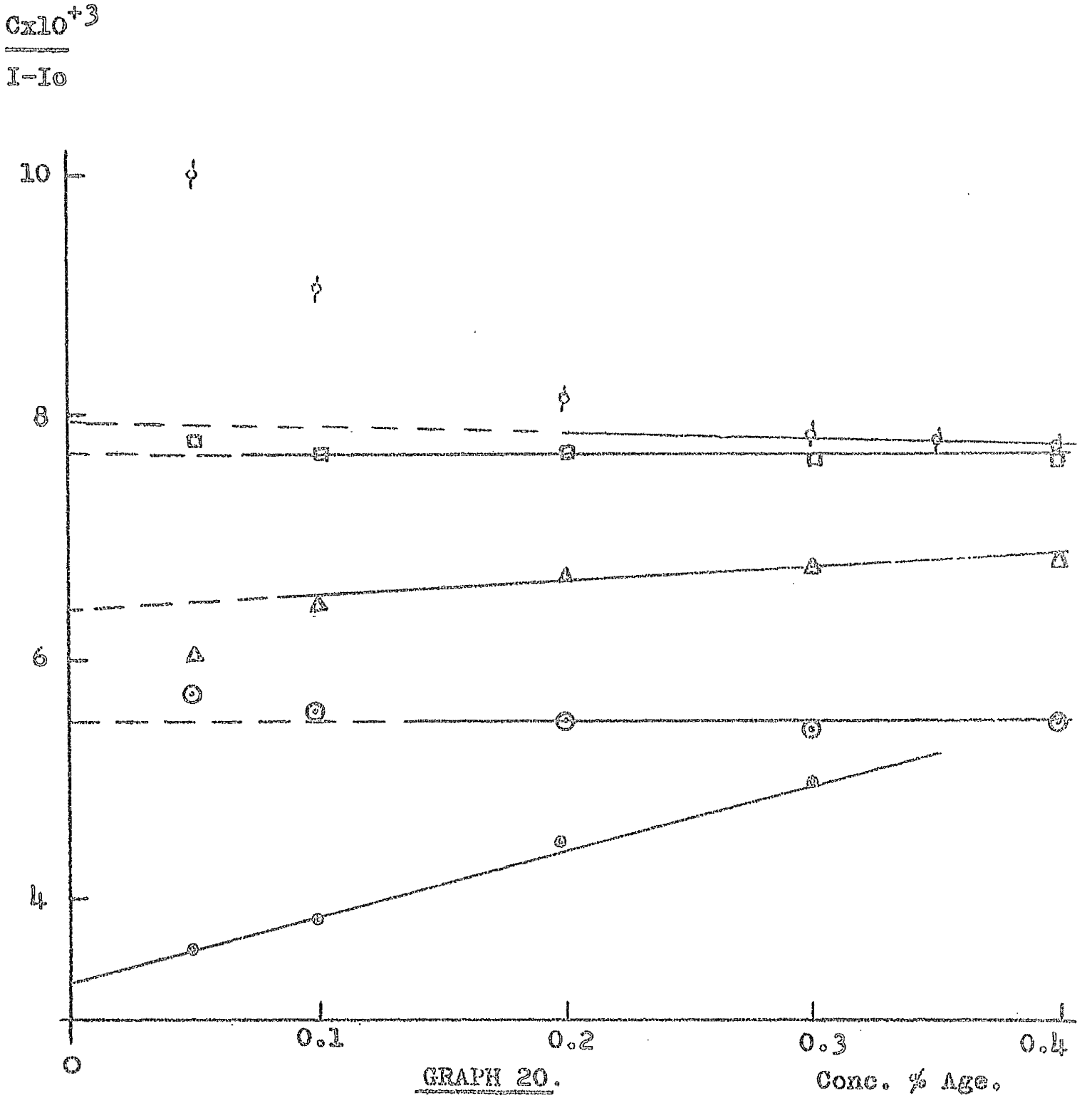
UNDECENYL TRIMETHYL AMMONIUM BROMIDE



GRAPH 19

UNDECENYL TRIMETHYL AMMONIUM BROMIDE.

NOTATION AS IN GRAPH 19



GRAPH 20.

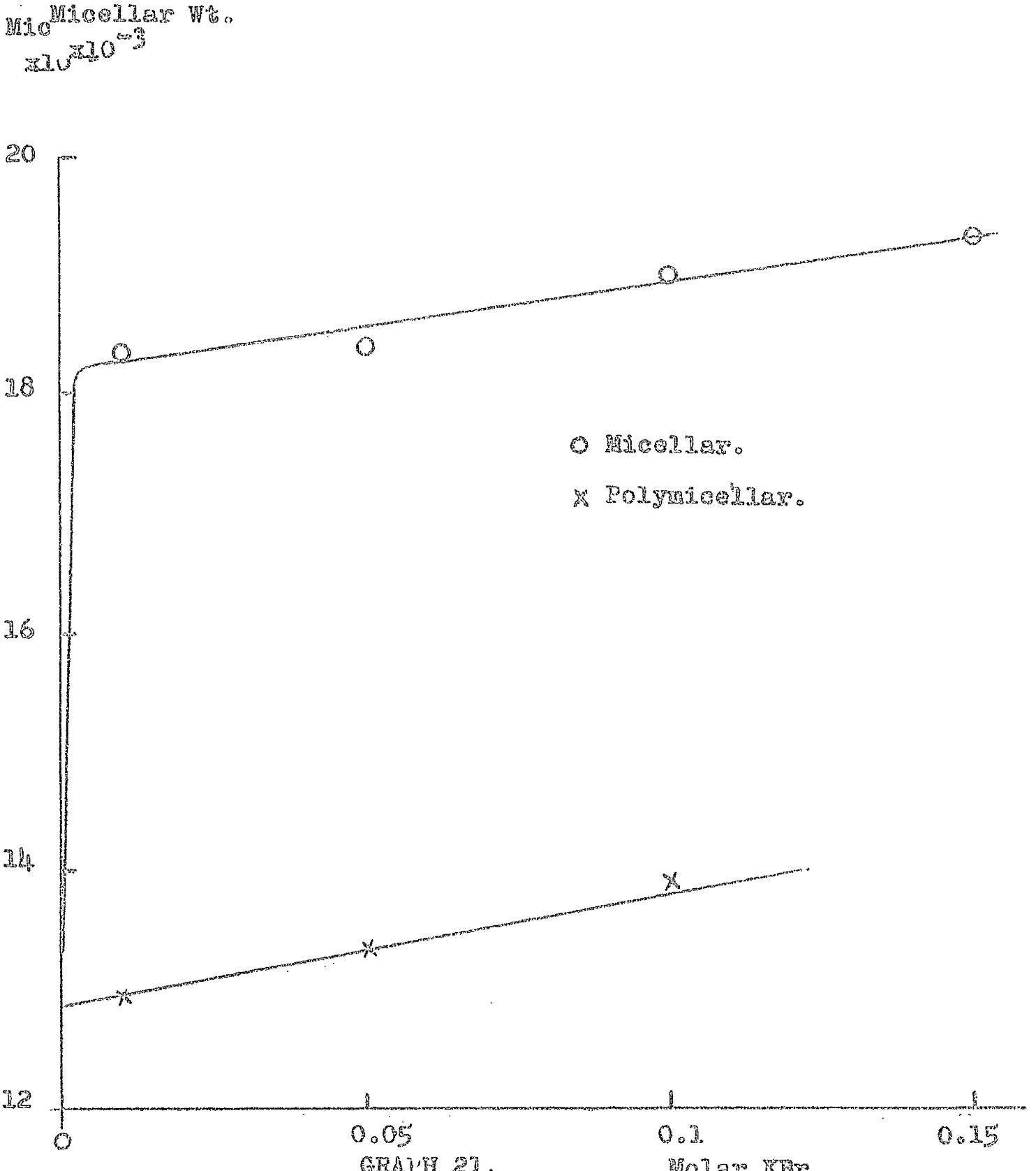
Values of $\left(\frac{dn}{dc}\right)_{\mu}$ electrolyte were obtained in an analagous manner to S.U.S. Inserting these values in the Debye equation gives a range of polymicelle weights which increase slightly (table 6) and extrapolate back to 12,850 (graph 21).

TABLE 6.

Conc. KBr. Molar	Lim. $\frac{C}{I-Io} \times 10^3$	$\left(\frac{dn}{dc}\right)_{\mu}$ electrolyte	M
0.01	5.47	0.167	12,950
0.05	6.4	0.152	13,350
0.1	7.68	0.136	13,900
0.2	7.95	0.134	13,850

In this instance there is much less unpolymerised soap, 5 to 6% escaping through the dialysis membrane. Also the extrapolated polymicellar weight of 12,750 is close to the apparent micellar weight of 13,300 indicating that most, if not all, of the molecules of which the micelle is composed

UNDECENYL TRIMETHYL AMMONIUM BROMIDE.



GRAPH 21.

have polymerised together in a manner suggested by fig. 4.

Using the correct $\left(\frac{dn}{dc}\right)_{\mu}$ electrolyte values for the polymicellar soaps in KBr leads to a reduction of 30 to 40% in the polymicellar weights compared with the corresponding micellar weights as obtained by conventional means. The difference is small (3 to 4%) in the case of U.T.A.B. in water. Remembering that there will be little or no change in polymicelle size with concentration of soap, the fact that their molecular weights are so similar could mean that there is little change in micelle size with soap concentration.

Undecyl Trimethyl Ammonium Bromide:-

In order to ascertain whether or not the presence of an olefinic bond in the paraffin chain of a colloidal electrolyte had made any significant difference to the apparent micellar weights compared with its saturated counterpart a series of light scattering measurements was conducted on undecyl trimethyl ammonium bromide. Plots of the induced intensity I-Io versus C in graph 22 show the

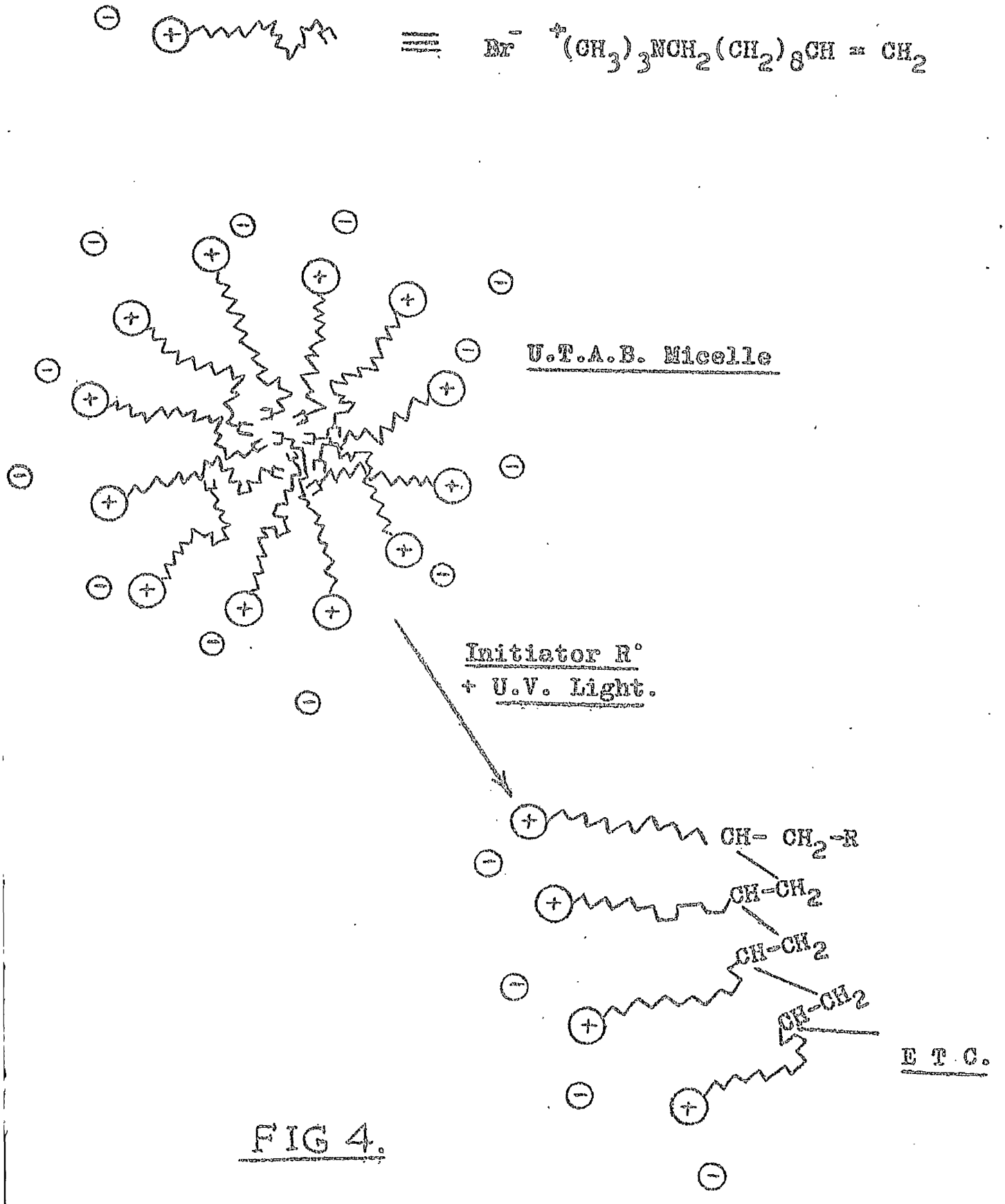
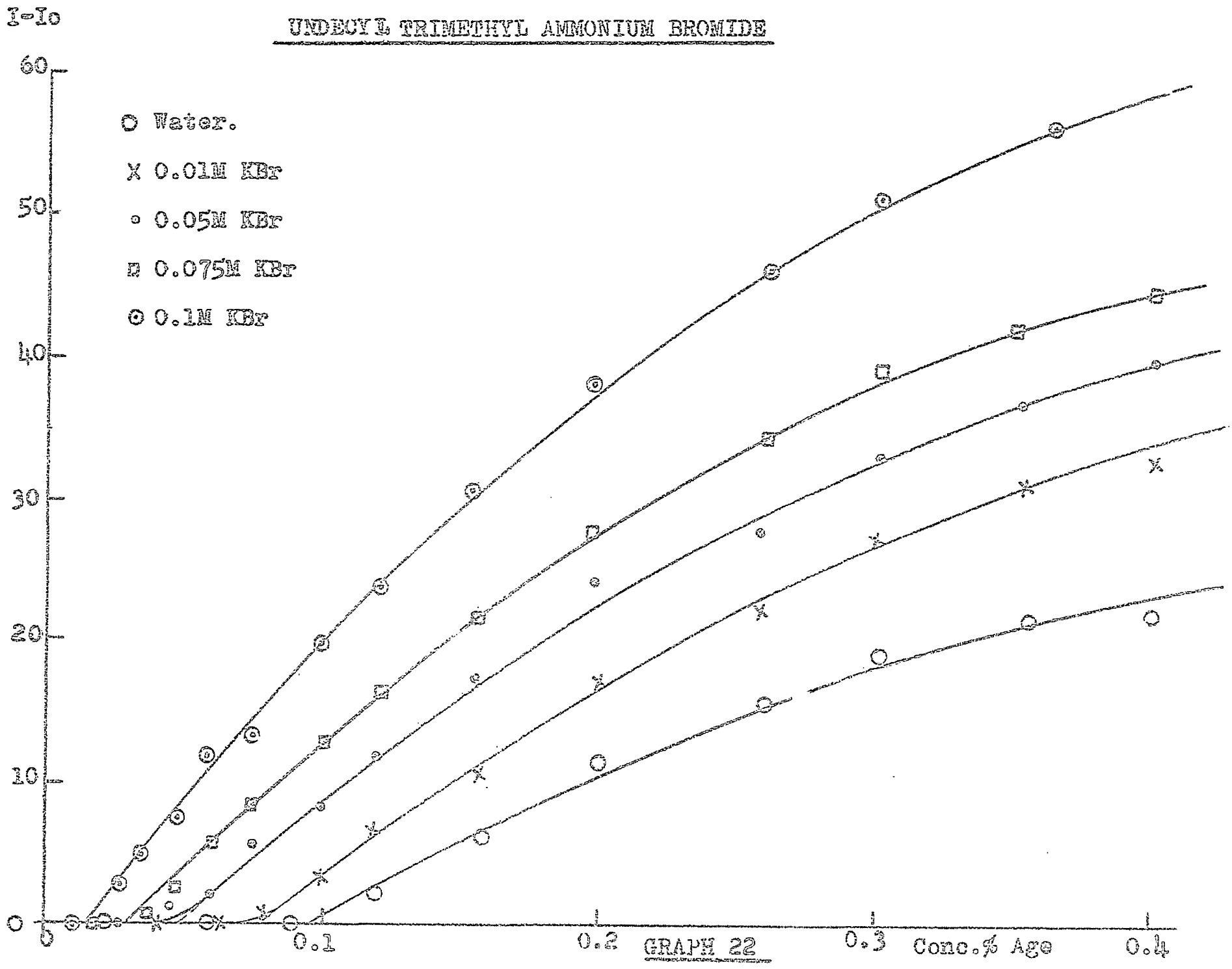

$Br^- \; {}^+(CH_3)_3NCH_2(CH_2)_8CH = CH_2$
U.T.A.B. Micelle
Initiator R°
+ U.V. Light.
CH- CH_2-R
CH=CH_2
CH=CH_2
CH=CH_2
E T C.

FIG 4.


I-Io
UNDECYL TRIMETHYL AMMONIUM BROMIDE
60
50
40
30
20
10
0
Water.
0.01M KBr
0.05M KBr
0.075M KBr
0.1M KBr
0
0.1
0.2
0.3
0.4
Conc.% Age

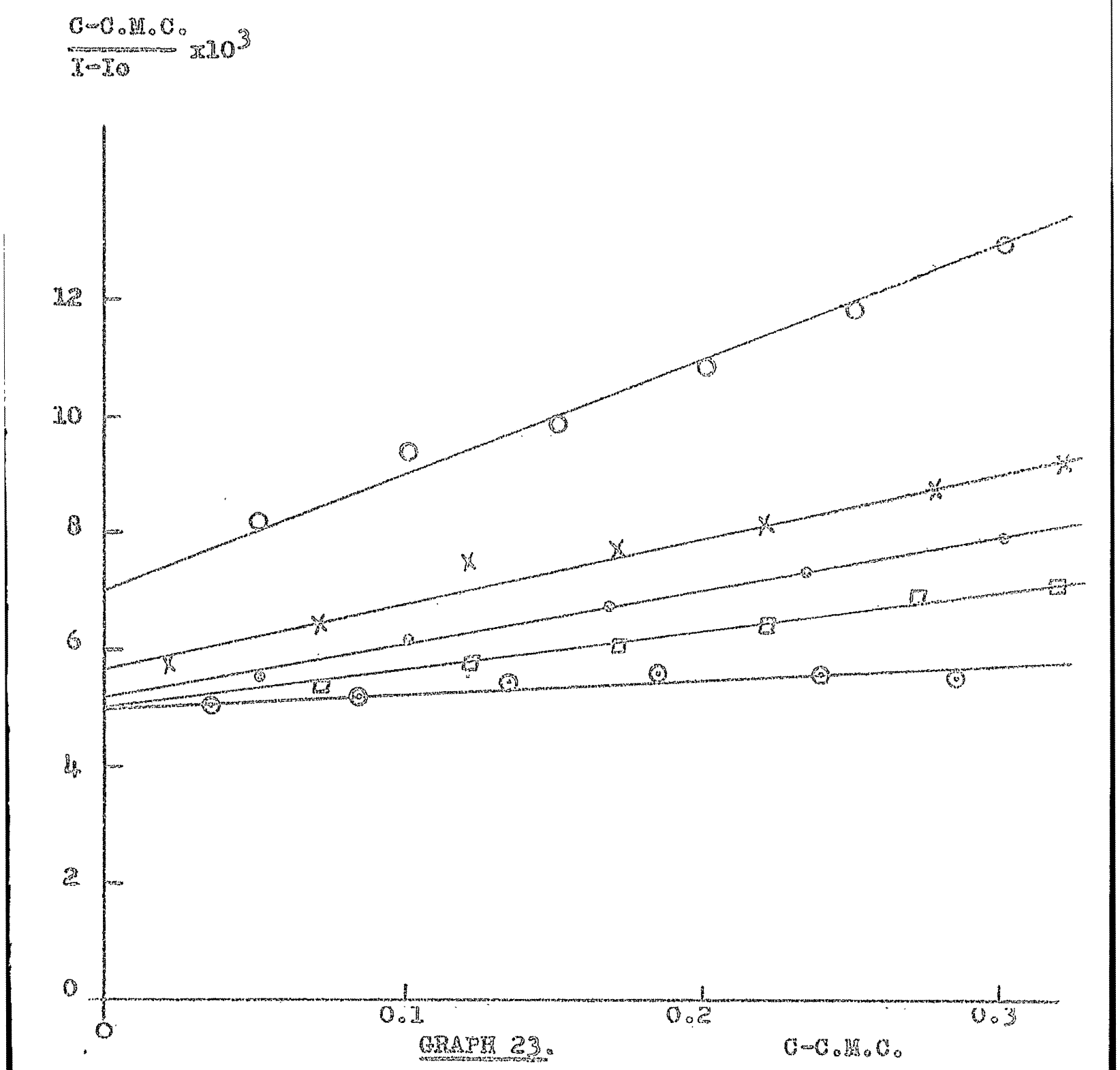
GRAPH 22

normal trends of an increase in scatter and decrease in the C.M.C. with increasing KBr concentration. The intercept values grom graph 23 along with respective $\left(\frac{dn}{dc}\right)_{\text{const. electrolyte conc.}}$ enable the apparent micellar weights to be calculated. These are summarised in graph 24. The value of 13,100 compares very favourably with that for the unsaturated soap (13,300). The errors incurred in both calculations (by neglecting charge effects) will be essentially the same, so there can be no doubt that the inclusion of a double bond in the paraffin tail of a detergent makes no significant difference to the apparent micellar weights. As with all the cases studied so far the apparent micellar weights increase with added electrolyte reaching a value of 16,000 independent of electrolyte concentration after about 0.02M.

The effect of electrolyte on the apparent micellar weight is more pronounced with the higher homologue soaps. With hexadecyl trimethyl ammonium bromide (H.T.A.B.) graph (25) it

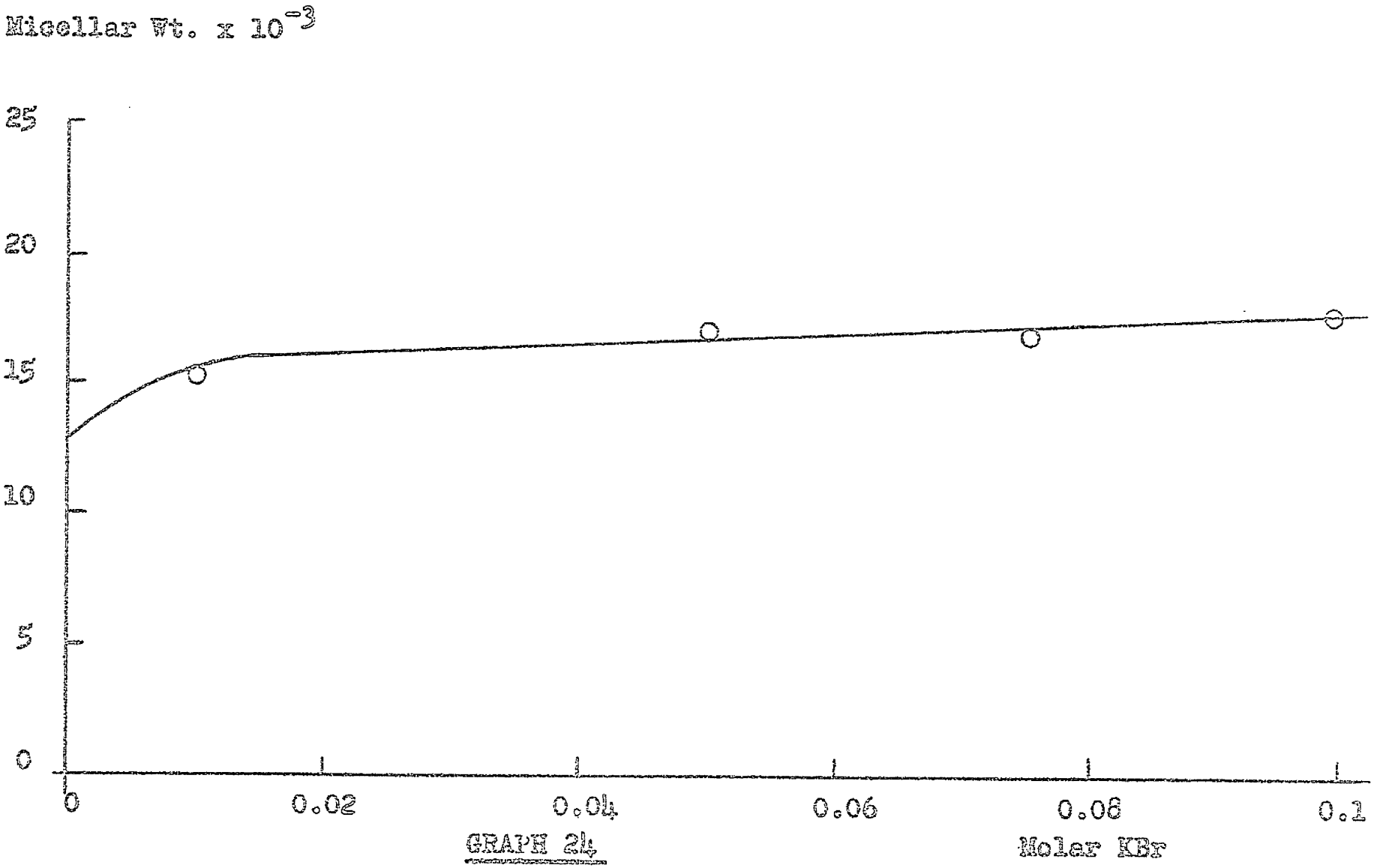
UNDECYL TRIMETHYL AMMONIUM BROMIDE.

NOTATION AS IN GRAPH 22



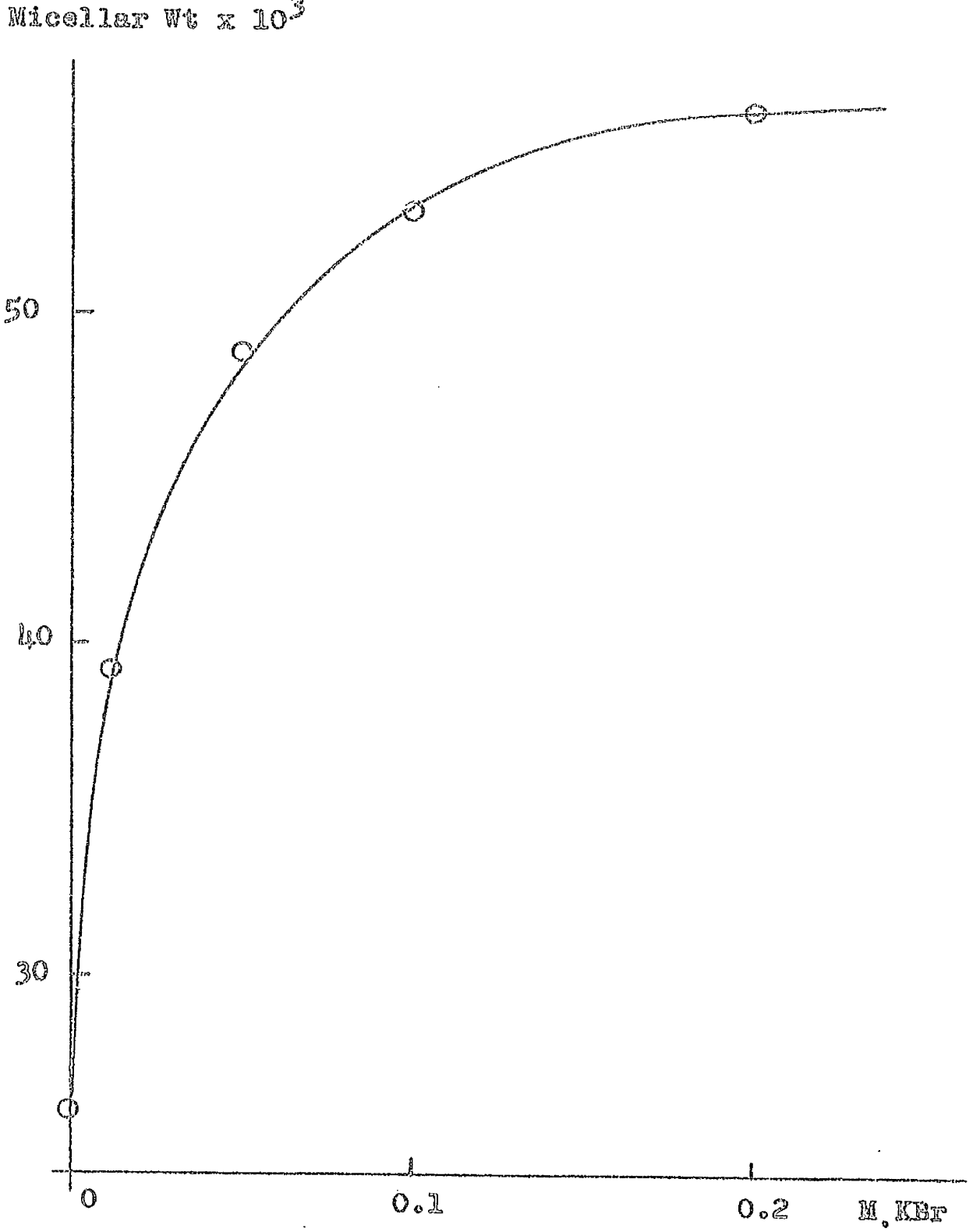
GRAPH 23.

UNDECYL TRIMETHYL AMMONIUM BROMIDE.



GRAPH 24

HEXADECYL TRIMETHYL AMMONIUM BROMIDE.



GRAPH 25

was found that the apparent micellar weight increased from 26,200 in water to 56,000 in 0.2MKBr. Also there is a decrease in the critical concentration with the increased number of CH_2 groups, coupled with an increase in the number of single molecules contained in the micelle.

Locus of Polymerisation:-

The fact that A.B.I.N. gives rise to two radicals $(CH_3)_2\overset{CN}{\overset{|}{C}}.$ per molecule and that the micellar weights evaluated from the polymicellar solutions all appear to be much lower than the values for the unpolymerised soaps, suggests that there may be more than one centre of polymerisation per micelle. To investigate this possibility 1.5 gms. styrene was solubilized in 150 ccs. of 3% H.T.A.B., initiator added and the solution irradiated with U.V. light for 5 hrs. On the basis of 72 molecules per micelle for H.T.A.B. this amount of styrene corresponds to 90 molecules per micelle. Thus if there is one centre per micelle polystyrene of

molecular weight 9,000 should be formed and half of this value if there are two centres which do not terminate by coupling. Irradiation for 5 hours caused a slight turbidity to develop in the solution. It was then mixed with a large excess fo methyl alcohol to bring about dissociation of the micelles and precipitate the polystyrene. The molecular weight of the polymer so formed was obtained by light scattering using benzene as solvent. Unfortunately polystyrene of molecular weight 500,000 resulted showing that there had been a transfer of growing polymer between micelles or a coalescence of micelles with those containing growing polymer, similar to emulsion type polymerisation. Reducing both the amount of styrene solubilised and the irradiation period still gave rise to high molecular weights. This simply showed that there exists a large difference between the polymerisation of a monomer in olefinic and saturated soaps. Presumably in the olefinic case the styrene copolymerises with the soap thus preventing it spreading thoughout the solution.

CONCLUSIONS:-

The project was initiated in order to try and eliminate some of the uncertainties encountered in the determination of micellar weights by light scattering in dilute solutions of colloidal electrolytes and allow for a more concise analysis in the light of present theory. It was thought that the possible formation of polymicelles from micelles would enable more accurate measurements to be made in dilute solutions where present work is made difficult by the lability of the micelles. In some cases the demand proved too heavy for the idea in that it tended to complicate instead of simplify the situation. While falling short of its original purpose many interesting results were found from a study of solutions of polymerised detergents.

The possibility that polymicelles, as envisaged above, could be formed with sodium oleate and solubilized styrene was thwarted by the formation of long chain polysoap, vastly different in chemical composition from the original micelles. This polysoap, which had a molecular weight dependent on the solubilized styrene concentration, was similar to that prepared by Strauss and his co-workers (71-75) (from poly-2-

-vinyl-pyridine, by quarterizing about $\frac{1}{3}$ of the nitrogen with dodecyl bromide). Approximately 45 oleate molecules entered into co-polymerisation with the styrene monomer to form polystyrene with oleate side chains attached.

The elimination of the breaks in the Λ versus $\sqrt{C}$ curves (at the C.M.C.) and the change in the (I-Io) versus C plot on irradiation both indicate that with S.U.S. there are few dissociable micelles left in solution. The Debye treatment (eq. 23) of the light scattering results with this detergent before irradiation gives an apparent micellar weight of 30,800 in water, rising to 54,200 in 0.2M Na_2SO_4. According to Prins theory (54), taking into account the charge and excluded volume effects, the value in water is slightly low and should be adjusted to 34,000, whereas the values in dilute electrolyte solution are correct, p being zero in eq.(27). Employing the $\left(\frac{dn}{dc}\right)_{\mu}$ electrolyte values, obtained from the dialysis experiments, (allowing for solute lost through the membrane) questions the validity of previous

micellar weight determinations where $\left(\frac{dn}{dc}\right)_{soap}$ c electrolyte has been used. There is a substantial difference between the two refractive index increments and it is not easy to see how one would be able to determine $\left(\frac{dc\ electrolyte}{dc\ soap}\right)_{\mu}$ in order to compute $\left(\frac{dn}{dc_{soap}}\right)_{\mu}$ electrolyte from $\left(\frac{dn}{ds\ soap}\right)$ c electrolyte and $\left(\frac{dn}{dc\ electrolyte}\right)$ due to the lability of the micelles.

The polymicellar weights obtained for S.U.S., both measured directly and by extrapolation of the solubilized styrene measurements , are in the region of 13,500 : much lower than the unpolymerised S.U.S. solutions. This is to be expected with incomplete polymerisation and the other possibility that there is more than one polyermisation centre per micelle and termination if predominantly by disproportionetion . The experiment with H.T.A.B. and solubilized styrene to investigate the possibility that there may be more than one centre of polymerisation per

micelle by using A.B.I.N. as initiator was unfortunately unsuccessful. The resultant polystyrene of molecular weight 500,000 showed that there had been a transfer of growing polymer between micelles or a coalescence of micelles with those containing growing polymer. This simply illustrated that there exists a large difference between the polymerisation of a solubilized monomer in olefinic and saturated soaps. Presumably in the olefinic case the styrene co-polymerises with the soap thus preventing it spreading throughout the solution.

The original hope of polymerising together the molecules in each separate micelle was almost realised with U.F.A.B. The change in the Λ versus $\sqrt{C}$ curves; the fact that light scattering can be detected below the C.M.C. of the unirradiated soap; the very small loss of solute on dialysis and the fact that the polymicellar weight of 12,750 is close to the original micellar weight of 13,300 all indicate that most, if not all, of the molecules of which the micelle is composed have polymerised together. Both of these results will

be subject to approximately the same corrections for charge effects, but one can conclude from their similarity that since the aggregation number of the polymicelles remains constant as the concentration is varied so there will be very little change in micellar size as the detergent concentration is varied.

There is a significant difference between the polymicellar and micellar weights of U.T.A.B. in dilute solutions of KBr. Conventional methods give rise to micellar weights of up to 19,700 in 0.2M KBr whereas these range from 12,950 in water to 13,850 in 0.2M KBr with polymicellar solutions. The difference lies in employing $\left(\frac{dn}{dc}\right)_{\mu}$ electrolyte in the scattering equation (23) which is thermodynamically the correct refractive index increment to use. Since it has been shown that there is no measurable difference between the micellar weights of undecenyl trimethyl ammonium bromide and undecyl trimethyl ammonium bromide it can be argued that previous micellar weight determinations in dilute salt solutions (22,23,29,52,53) for

saturated cationic and anionic detergents are in error. Technically the only way of correcting these results is by using the dialysis method which is only available for polymerised soaps, where the micelles are prevented from dissociating.

Other well established features of micellar solutions were further corroborated. The C.M.C. decreases with added electrolyte and is lower for the higher homologue soaps (U.T.A.B. CF H.T.A.B.) The absence of dissymmetry in all cases shows that the greatest dimension of the micelle remains below 200 A°. In theory the depolarisation of the light scattered at 90° may also give some information as to the asymmetry of the micelles. However in almost all cases the depolarization was very small and probably due to the disturbing influence of dust in the solutions.

PART II.

SOLUBILIZATION OF SOME ORGANIC ADDITIVES BY HEXADECYL TRIMETHYL AMMONIUM BROMIDE.

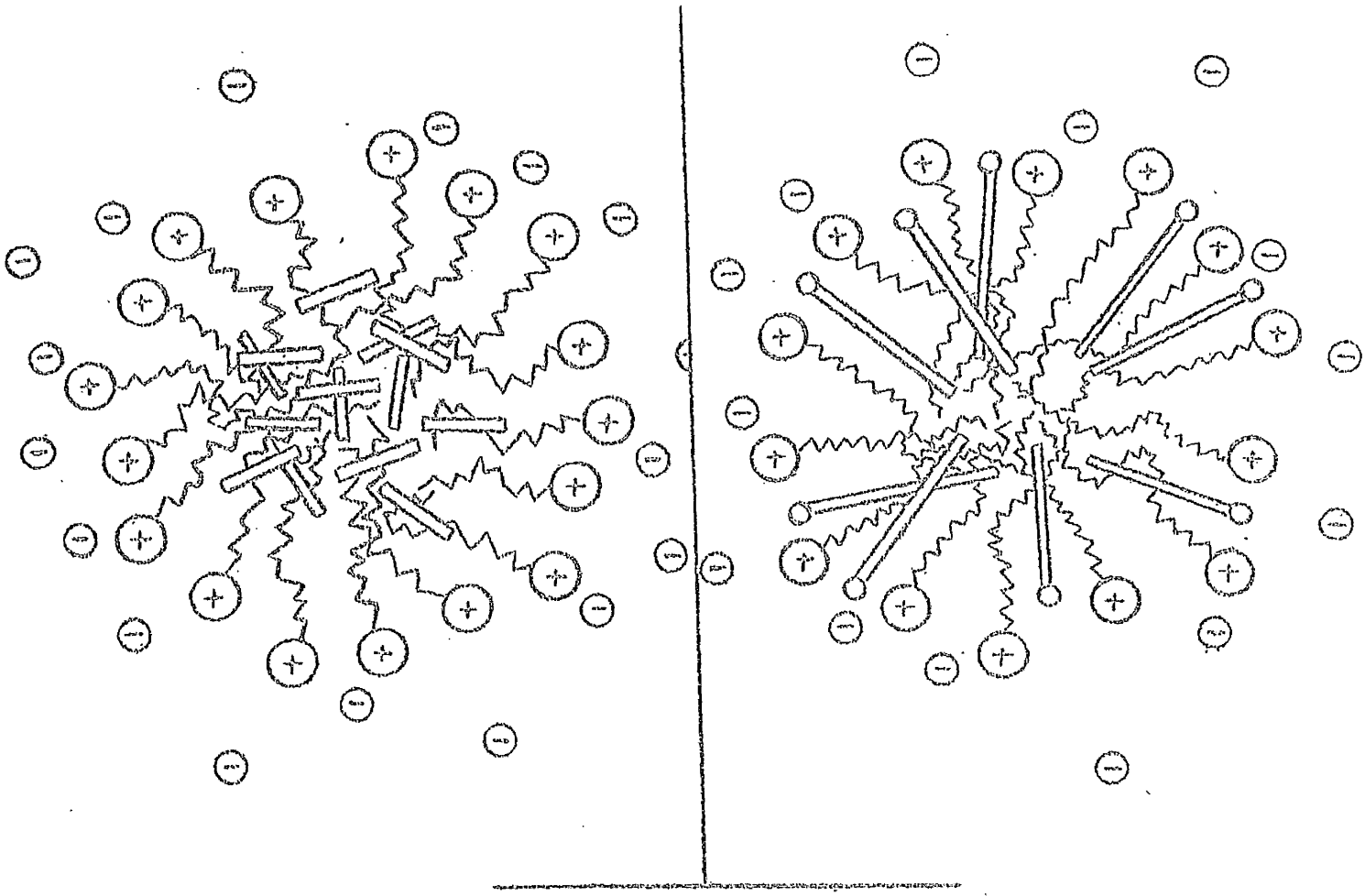
INTRODUCTION.

General:-

The ability of detergent solutions to dissolve organic compounds, insoluble or only slightly soluble in water, is one of their striking properties called solubilisation. Little uptake is found until the C.M.C. is reached, indicating that the compounds are taken up in some way by the micelles. It is generally believed that with non-polar hydrocarbons uptake occurs by solution in the interior of the micelle and with partly miscible polar compounds such as hexanol, long chain amines and phenols by adsorption into the micelle surface with the hydrocarbon part inside and the polar group in the aqueous phase. The probable structures in the two cases are shown schematically in fig (5).

The saturation limit of solubilization of a liquid by a

SOLUBILIZATION WITHIN MICELLES.



Paraffin Chain Electrolyte.

Associated Cegenion.

Non Polar Hydrocarbon.

Polar Compound.

FIG 5.

colloidal electrolyte solution may be followed conveniently in terms of the optical density of the solution. In general, organic liquids are readily emulsified by colloidal electrolytes and this may be utilized to show when saturation is reached. A given volume of detergent solution is shaken up at constant temperature with organic liquid and from the absence or presence of opalescence at the end of several hours it can be seen whether or not all the added liquid has dissolved. By preparing a series of samples containing increasing amounts of organic liquid inspection by eye if often sufficiently accurate to determine the saturation end point. Alternatively a more accurate estimation may be made instrumentally, either by transmission measurements (76), or by light scattering (77).

Previous work on Solubilization in Ionic Detergents:-

No quantitative information is available to show how much expansion the micelle of ionic detergents suffers as a result of solubilization but Ralston (78) has shown that the mobility of the micelle undergoes change. He found that when

n-hexane, benzene and cyclohexane are solubilized in an aqueous solution of dodecylammonium chloride their presence brings about an appreciable lowering of the conductivity of the colloidal electrolyte. All three of these hydrocarbons appear to lower the C.M.C. which suggests that they assist in micelle formation. The affinity of the additives for the hydrocarbon portion of the associated ions is underlined by the 'infinite' solubility of benzene and cyclohexane in dodecane(79). The higher straight chain hydrocarbons octane, dodecane, heptadecane and octadecane have less effect on the conductivity than the 6 membered hydrocarbons and the lowering of conductivity decreases progressively with increase in chain length. This shows that an increase in chain length of the hydrocarbon is attended by a reduction in its ease of solubilization and is in conformity with the findings of McBain and Richards (77) that hydrocarbons of high molecular weight are scarcely solubilized. Ralston (78) also found that the higher alcohols

hexanol, octanol, dodecanol and octadecanol have a profound influence upon the conductivity of dodecylammonium chloride but no effect on solutions of hexylammonium chloride. Since the latter salt has been previously shown (79) to function as an ordinary electrolyte, even in concentrated solutions, we can assume that the effects noted with the additives in dodecylammonium chloride are due to its colloidal nature.

By using a pinacyanol chloride dye to detect the C.M.C. Klevens(80) reported a very small decrease in the C.M.C. of soap solutions on the addition of benzene. The amount of benzene in the micelle is not determinable, because the distribution of benzene between micelle and water is not known in the vicinity of the C.M.C.. The decrease is much greater with the higher alcohols, as reported by Shinoda(81) and Ooshika(82). These authors explain the decrease in C.M.C. in terms of a decreased charge density in the micelle surface and the decrease in free energyof mixing. Schick(83) attributed this lowering of the C.M.C., on the incroporation of long chain

polar molecules into the palisade layer of micelles, to a lowering of the activity of the detergent molecules and an increase in the attractive van der Waals forces between the molecules.

Mersfeld et.al.(84) have indicated the likelihood of a reconstitution of a micelle formed in the presence of a long chain alcohol. He points out that it is reasonable to expect that the repulsive potential between the polar head groups in the micelle would be altered in the presence of the alcohol; this would lead to a variation in the number of long chain ions per micelle as some unknown function of the alcohol concentration.

It is evident from the many different aspects of solubilization which have been investigated (76,77,80,85,86-102) that the major factor which controls the amount of material solubilised in a given system is the chemical compositon of the detergent and the solubilizate. There appears to be no

definite relationship between the solubilizing power of an ionic detergent and theproperties of the solubilizate such as molecular weight, molecular volume, chain length and polarity. All the investigations listed above lead to a great amount of speculation but qualitatively at least the following conclusions may be drawn:-

1. No quantitative information is available to show how much expansion the micelle suffers as a result of solubilization.
2. the mobility of the micelle undergoes change as a result of solubilization (78).
3. the polar compound penetrates the surface of the micelle and has its polar head in more or less the same plane as the polar or ionic heads of the colloidal electrolyte (94,95,96), whereas non polar additives are to be located in the micelle.
4. in any homologous series of organic additive the extent of solubilization in a soap decreases as the chain length of the solubilizate increases (70,73).
5. an increase in the polarity of the solubilizate leads to an increase in the extent of solubilisation e.g. n-heptanol is solubilised more strongly than heptane (90,94).

6. the addition of KCl to potassium myristate solutions in the presence of small amounts of n-heptane and n-octanol enhances the solubility of the former and decreases that of the latter. (100).

The foregoing results are completely empirical on the quantitative level. Relationships between the extent of solubilization and molar volume (76), which appear to hold for a few members of a given homologous series seem to break down even in that homologous series when sufficient members are considered and different homolgous series appear to bear no quantitative relation to others.

Previous Work on Solubilization in Non-Ionic-Detergents.

Information concerning the change in the properties of micelles of non ionic detergents accompanying solubilization has been gathered by Nakagawa and co-workers (103). The surface active agents used in their experiments were methoxyoctaoxyethylene decyl ether $C_{10}H_{21}O(CH_2CH_2O)_8CH_3$ and methoxyundecaoxyethylene decyl ether $C_{10}H_{21}O(CH_2CH_2O)_{11}CH_3$.

n decane, which may be incorporated in the hydrocarbon interior of the micelle, and n-decanol, which penetrates into the palisade layer of the micelle, were used as solubilizates. In studying these systems by light scattering these workers found that there existed a sharp peak in the reduced intensity versus concentration curve at low concentrations. The peak appeared to be higher the larger the amount of solubilizate. This phenomenon had previously been found by Phillips and Mysels (104) in solutions of sodium dodecyl sulphate containing some dodecanol. The appearance of a peak is attributed to the formation of small droplets of excess solubilizate, when the micelles dissociate, which scatter a large amount of light. The values for Co were obtained from the extrapolated intercept of the I_{90} versus concentration curve. By applying the conventional Debye technique, mentioned in Part I, the micellar weights were calculated from plots of $\frac{H(C-Co)}{I-Io}$ V's (C-Co). It was found that the C.M.C. decreased and the apparent micellar weight increased with increasing amount of solubilizate in all

cases. The increase in micellar weight is accounted for, not only by the incorporation of solubilizate molecules, but also by an increase in the aggregation number of the nonionic agents themselves. In other words solubilization proceeds with a reorganisation of the molecules in a micelle. Their results also indicate a significant difference in the effect of decane and decanol on solubilization. The substantial difference between these two types of solubilization is further evidenced by the effect of added salt on the equilibrium solubilization values for ionic detergents (65,105). Salt increases the solubilization of hydrocarbons but greatly decreases the solubilization of long chain alcohols.

Purpose of this Work:-

Many of the conclusions drawn from solubilization data in colloidal electrolytes presuppose that the association factor does not change as a result of solubilisation. As has been shown in the case of the non ionics(103) there is reason to doubt this supposition. There is also the difficulty of distribution coefficients for the micelle/aqueous solution equilibrium. Data for the small aqueous solubilities of many of the solutes discussed is lacking. The question also arises, can we assume that the solubility of a hydrocarbon, or any other solubilizate,

in the aqueous phase of a micellar solution is the same as in pure water?.

In spite of the uncertainties mentioned in part I of this thesis as to the interpretation of the results evolved from light scattering measurements it was thought that experiments in which some hydrocarbons and long chain alcohols were solubilised in H.T.A.B. would give at least qualitative information concerning the change in constitution of micelles accompanying solubilization. As examples of straight chain paraffins octane and decane were used with benzene and cyclohexane as unsaturated and saturated cyclic hydrocarbons. The penetration type of solubilization into the palisade layer was studied by using octanol and decanol as solubilisates. The only additive to show any appreciable water solubility is benzene (0.171 gms./100 ml.water at 25°C (106)). An attempt was made to determine the distribution coefficient between benzene in the micelle and benzene in the aqueous medium by thoroughly mixing varying amounts of benzene in water paraffin mixtures. The quantity of paraffin employed was equivalent to the paraffinic interior of the H.T.A.B. solutions. The benzene

content in the water could be easily determined by optical density measurements on a Unicam spectrophotometer and calculating the results from a calibration curve.

Hyde and Lawrence (107) have studied the effects of the organic additives phenyl ethyl alcohol, m-cresol, aniline, benzene, ethyl benzene, n-amyl alcohol, t-amyl alcohol and n-butyl alcohol on the conductivity of hexadecyl trimethyl ammonium bromide. They conclude from the experimental results that there are two types of solubilisation, one for semipolar and one for apolar molecules. They attributed the increase in Λ in the former case as due to the soap ions being located further apart on the penetrated surface so that the micelle can part with some of its gegenions which were previously closely bound. Other deviations in slope in the Λ versus concentration of additive were attributed to changes in the shape and size of the micelle.

Thus, as a continuation of the above study, the work in this section was devoted to the investigation of solubilized solutions

of hydrocarbons and alcohols in H.T.A.B. by light scattering. Some experiments on sodium undecenyl sulphate solutions were also carried out with styrene as additive so that they might be compared with some experiments where the styrene and soap had been copolymerised (Part I).

EXPERIMENTAL.

As a precautionary step the commercial H.T.A.B. (Hopkin and Williams) was purified by extraction with ether in a soxhlet extractor. Further recrystallisation from methyl ethyl ketone gave a compound with a satisfactory combustion analysis.

ACTUAL	%C	= 61.08	THEORETICAL	%C	= 62.0
	%H	= 11.1		%H	= 11.5.

Titration of the bromide in 80% ethanol with $AgNO_3$ gave a value greater than 99% theoretical.

The sodium undecenyl sulphate was synthesised from undecanol as mentioned in part I.

The hydrocarbons (benzene, cyclohexane, octane and decane) and the long chain alcohols (octanol and decanol) were all good quality reagents and were used without further purification. The styrene was prepolymerised, the pure monomer being distilled off under vacuum.

A series of samples containing 20 ccs. 1% detergent and increasing amounts of organic additive (introduced using a calibrated Agla micrometer syringe) were sealed in glass tubes

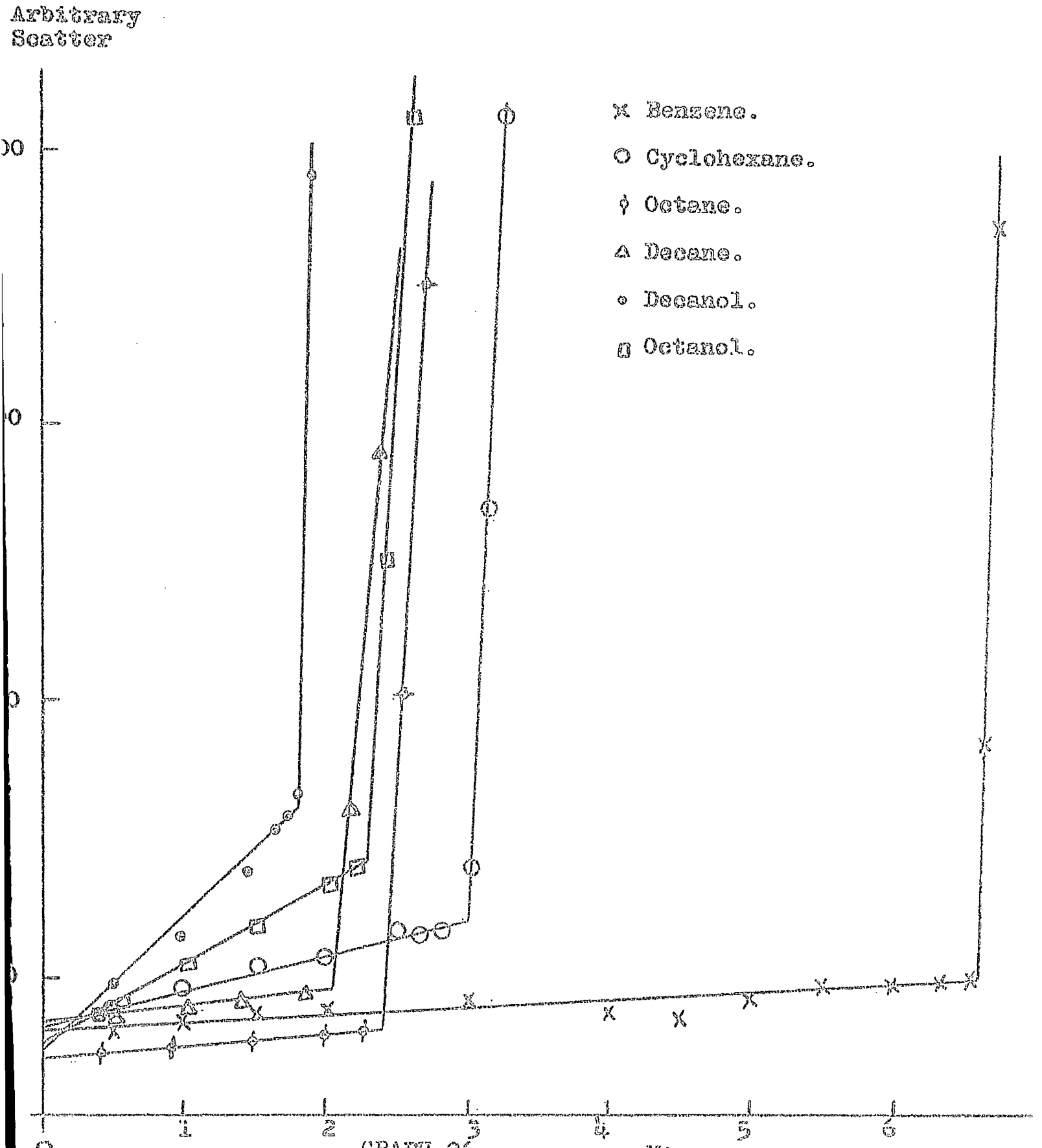
and thoroughly mixed by rotation, submerged in a thermostated bath at 25°C. Anestimate of the saturation end point was made by the visual onset of opalescence. Addition of small increments of the additive above and below the observed end point, followed by solubilization, enabled a more accurate estimation to be made by light scattering. Various amounts of the additive were dissolved in 100ccs of 1% detergent under the solubilization limit and the solution as a whole, after equilibration in the thermostat, diluted with water to give a series of concentrations suitable for light scattering. The water was deionized on a mixed bed ion exchange column and passed through a millipore filter. All the solutions were clarified prior to the scattering experiments by centrifugation at 30,000 G for 1 hr.. As before specific refractive index increments were measured using both a Rayleigh and Jamin Interferometer. The light scattering experiments were carried out using the apparatus marketed by S.O.F.I.C.A. explained in detail in part I. Scattered light was measured at 45,90 and 135° to the incident beam.

In the case of benzene, the only additive to show an appreciable water solubility, an attempt was made to determine the distribution of the additive between micelle and water. Mixtures with the same paraffin content as a 1% H.T.A.B. solution were made by adding 0.678 gms. of decane to 100 c.c.s. water. The paraffin, after vigorous shaking, separates from the water on standing (3 days) and has no effect on the optical density as determined by a Unicam spectrophotometer. Increasing quantities of benzene were added to these mixtures and the whole treated as the solubilized systems. After separation had taken place a sample of the aqueous layer was extracted and its O.D. measured at 200 m.μ. This was directly translated into amounts of benzene by means of a calibration curve. The O.D. measurements were extremely accurate and executed at high dilution.

RESULTS AND DISCUSSION:-

Having roughly determined the solubilization limit for each additive in 20 c.c.s. 1% H.T.A.B. an accurate measure of the value at 25°C was obtained by plotting the artitary intensity of scattered light at 90° to the incident beam versus the amount of additive as readings on the Agla syringe (graph 26). The rapid increase in scattered intensity corresponds to the limiting amount of additive which can be dissolved. The slight increase in turbidity before this critical point, observed in all cases, may be attributed to an enlarging of the micelle by solubilization. With the two long chain alcohols the small increase was greatly reduced by increasing the temperature of the solutions by only a few degrees. Indeed visibly cloudy solutions of H.T.A.B containing excess alcohol became optically clear on warming. Thus it appears that even at concentrations of alcohol below the apparent saturation point there are a number of molecules which are not completely solubilized at 25°C. Even an extremely small concentration of these molecules is sufficient to emulsify

SOLUBILIZATION LIMITS.



GRAPH 26.

with the ocean of water and cause an increase in the light scattered. These solutions are perfectly clear to the naked eye and this effect can only be detected instrumentally. Thus there exists a substantial difference between the saturation limit as determined visibly and instrumentally.

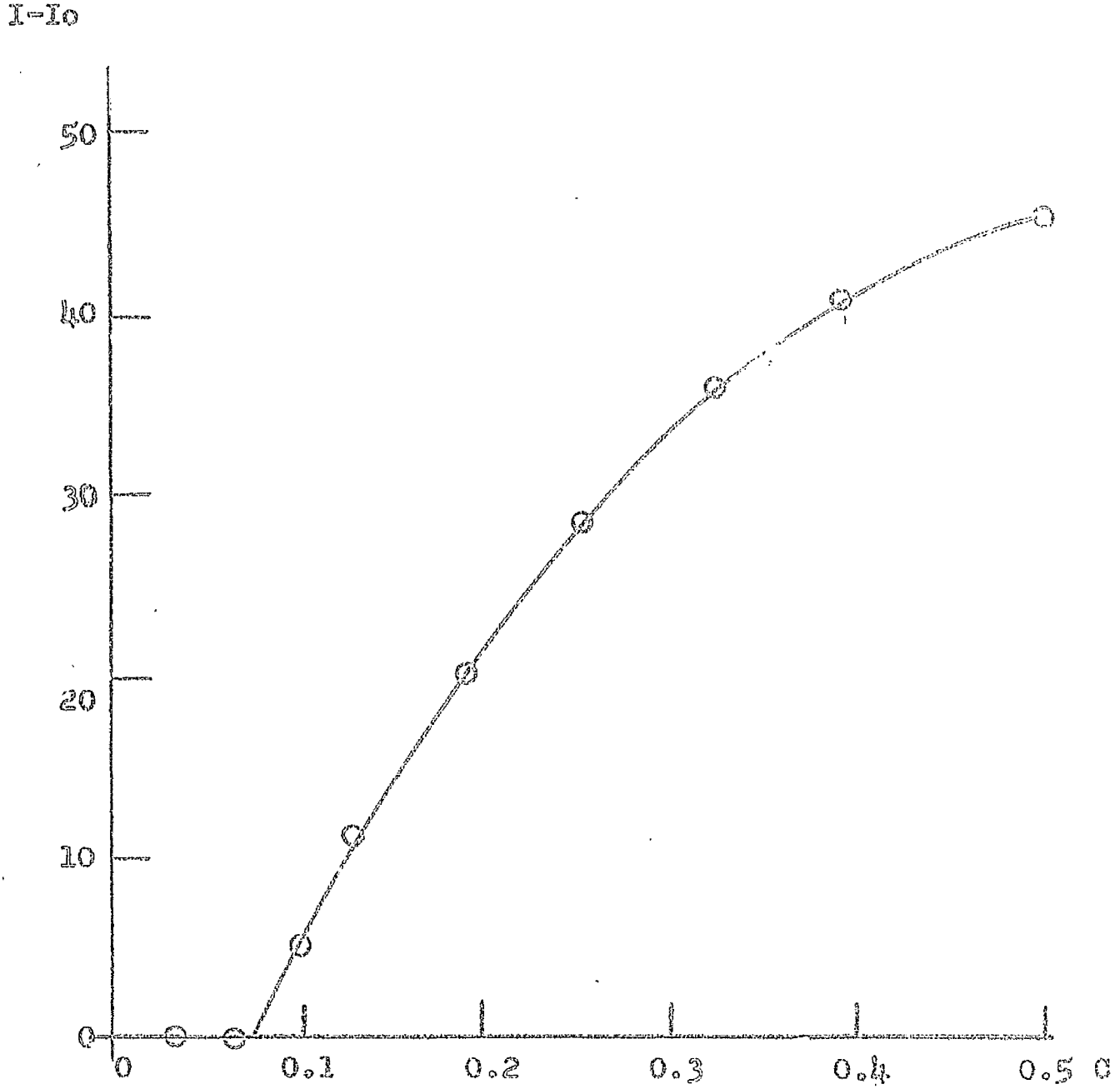
The difficulty now arises in the definition of the saturation limit of solubilization. It would appear from the saturation measurements that, in the case of the alcohols, solubilization as defined earlier is incomplete . One can surmount this difficulty however by defining the solubilization limit as that point where further addition of the additive causes a dramatic increase in the turbidity of the solution as determined by the amount of light scattered by the solution. On the basis of this definition the total amounts of additive, in grams, which can be solubilized in 100 c.c.s. 1% H.T.A.B. at 25°C are as follows:- benzene 0.485; cyclohexane 0.205; octane 0.165; decane 0.140; decanol 0.143 and octanol 0.181. The claim of Harkins and Oppenheimer(94) that an increase in the polarity of the solubilizate leads to an increase in the extent of solubilization is not evidenced here.

Decanol and octanol, presumably by penetration into the palisade layer of the micelle, are solubilized to approximately the same extent as their analogue hydrocarbons. Even taking into account its relatively high water solubility (0.171gms/ 100 ml.) and its low molar volume (88.5 C.F. 163.3 for octane) benzene seems to be solubilised to a greater extent than any of the other additives. This enhancement of solubilization due to the presence of double bonds has been noted by other workers (90,76,108)). There is the possibility that benzene due to its polarizability can be solubilised by a dual mechanism involving both the micelle interior and its palisade layer.

Addition of Octane:-

Graphs (27 A,B,C and D) give the reduced intensity of scattered light measured during the dilution of solutions of mixtures of H.T.A.B. and octane of varying compositions below the saturation limit for solubilisation. The curves of (I-Io) versus C are similar to that for the pure soap at high

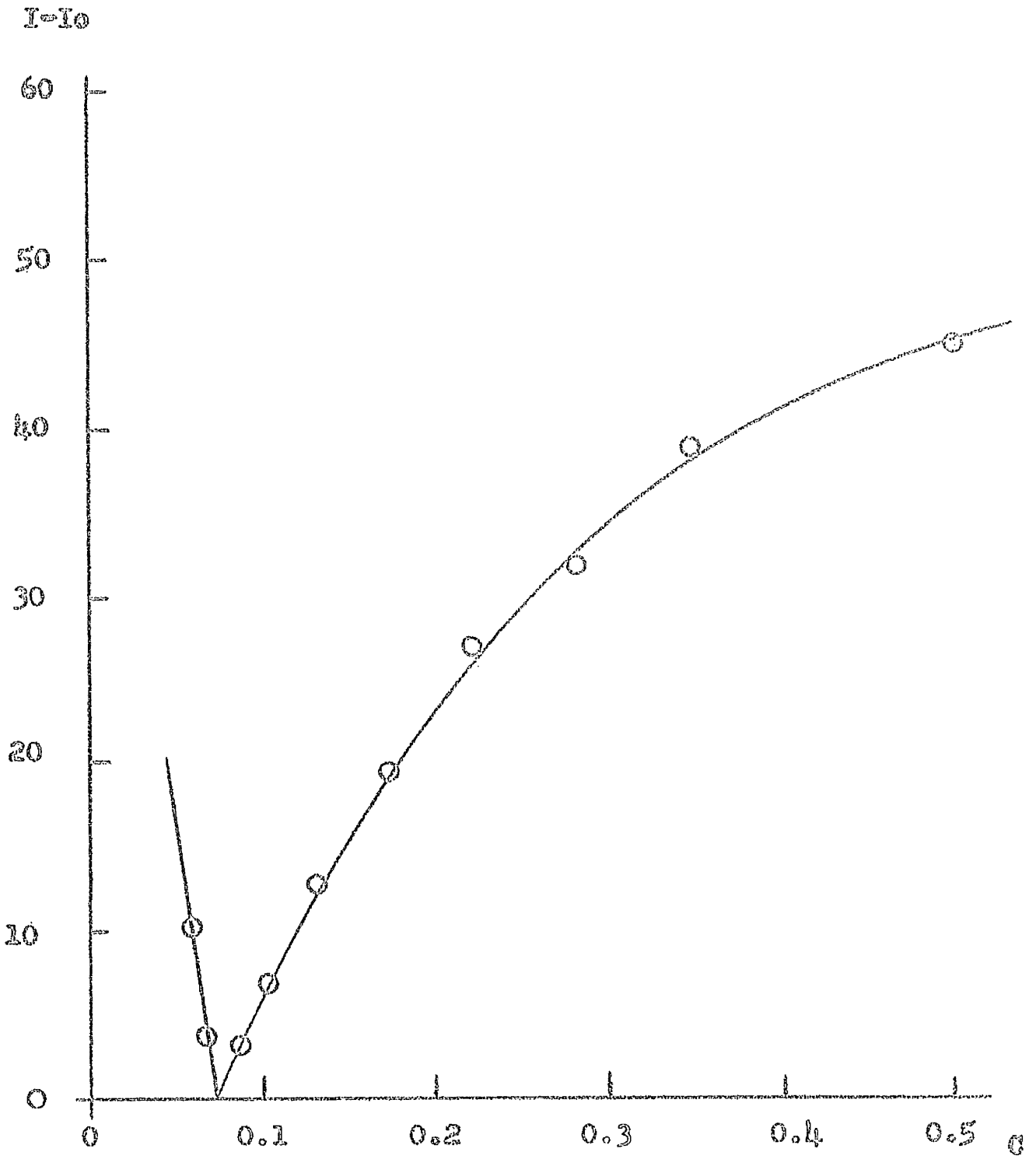
H.T.A.B. IN WATER.



GRAPH 27.

HEXADECYL TRIMETHYL AMMONIUM BROMIDE WITH OCTANE

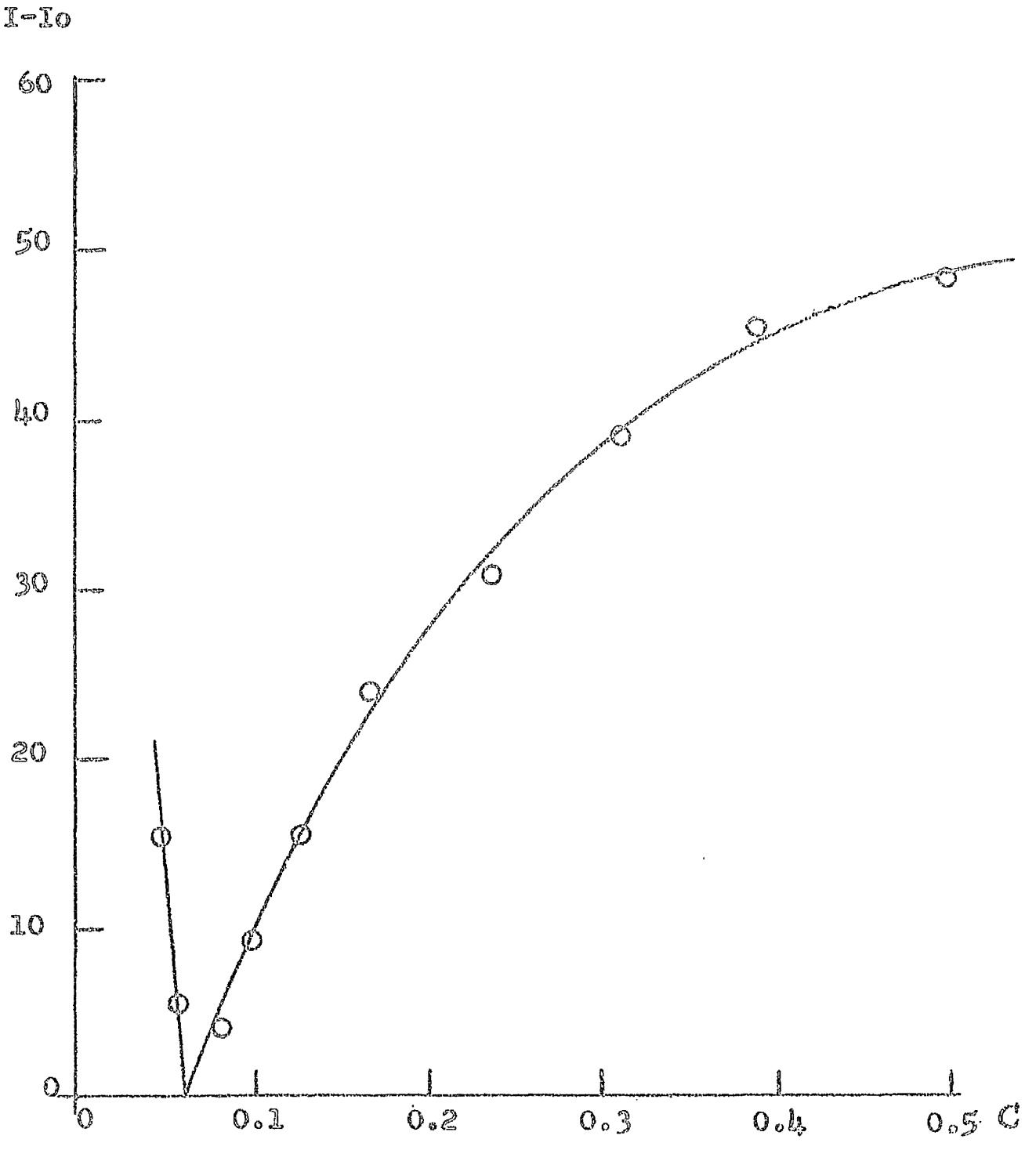
0.0198gms./100 ml. 1%



GRAPH 27A.

HEXADECYL TRIMETHYL AMMONIUM BROMIDE WITH OCTANE

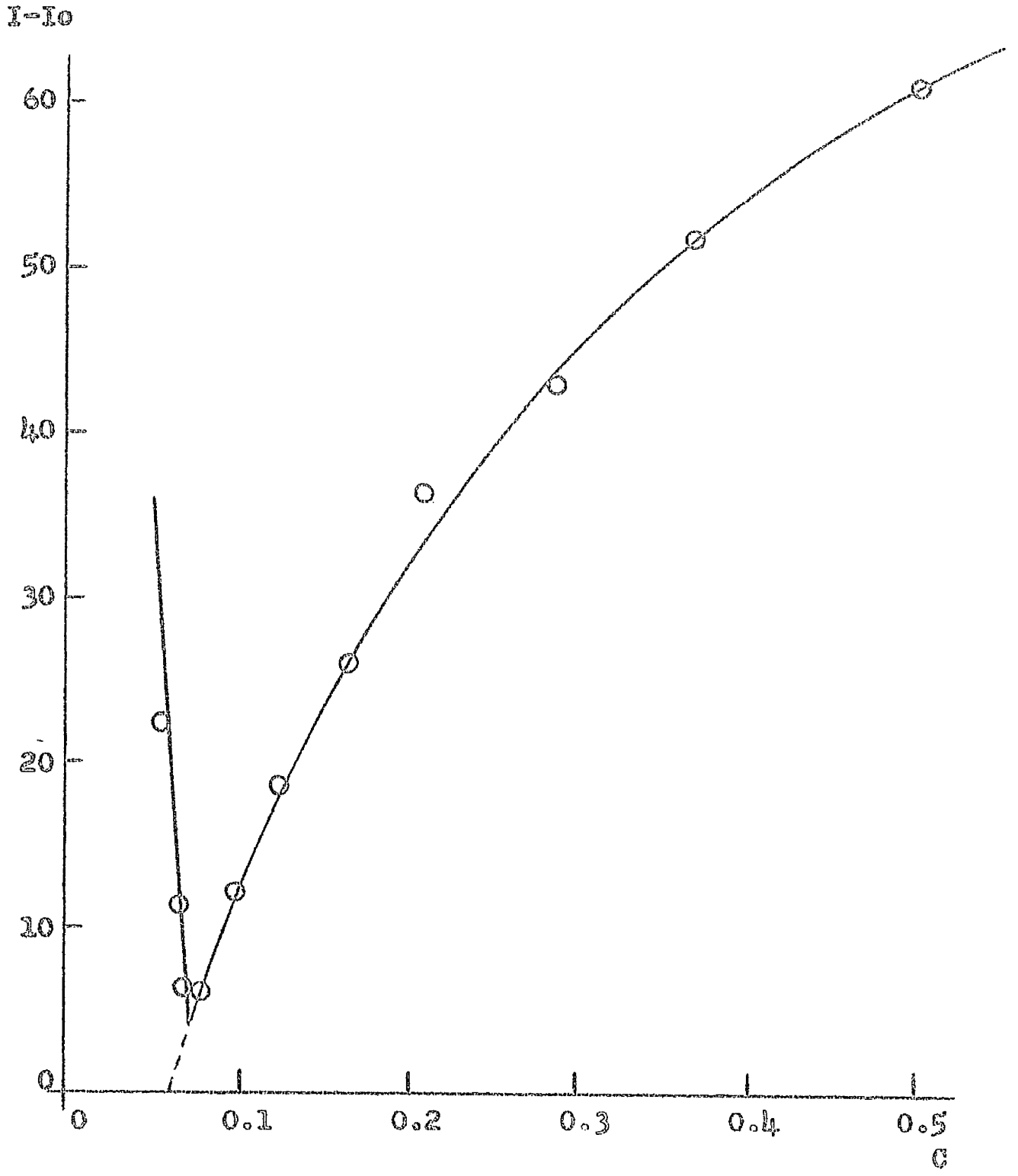
0.033 gms./100 ml. 1%



GRAPH 27B

HEXADECYL TRIMETHYL AMMONIUM BROMIDE WITH OCTANE

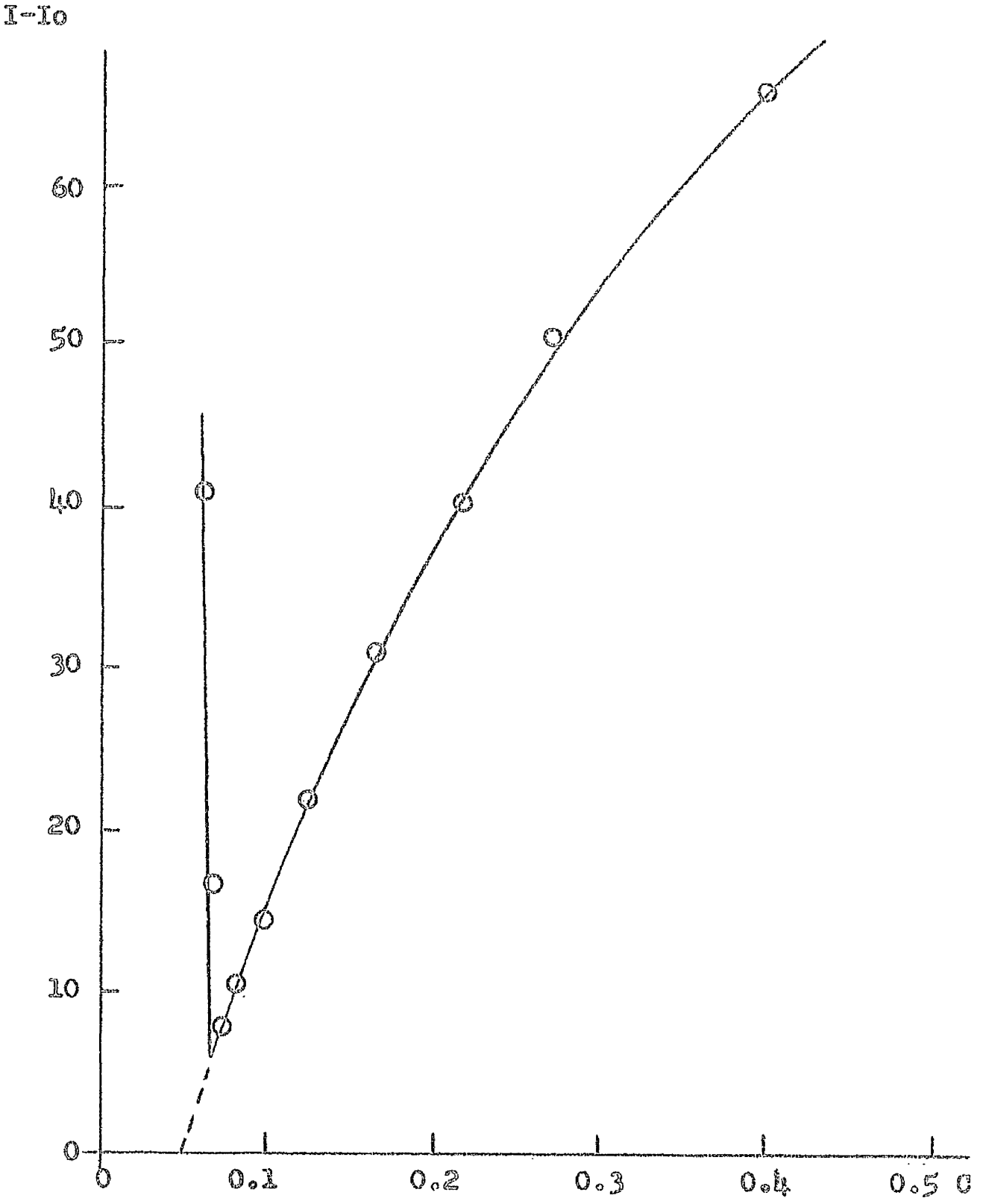
0.066 gms./100 ml. 1%



GRAPH 27 C

HEXADECYL TRIMETHYL AMMONIUM BROMIDE WITH OCTANE

0.099 gms./100 ml. 1%



GRAPH 27D

concentrations but an increase in scatter is observed with increasing octane content. At a fairly sharply defined point however the scattering intensity increases rapidly as the soap concentration decreases. By means of careful dilution sufficient points were obtained just before the break point to enable an accurate extrapolarion back to the concentration axis; to the point which must correspond to the C.M.C. for ordinary soaps. The vase increase in scatter is probably due to previously solubilized hydrocarbon aggregating when the micelles dissociate to give droplets which scatter a large amount of light. Mysels(10b) has argued that the C.M.C. in this case will be defined by the maximum of the peak formed at these low concentrations. Efforts to locate this peak were found to be futile, there being no reproducibility in the points obtained. This is reasonable considering the instability of the systems in this region. The fact that the scatter increases rapidly after the break point means that the dissociation into monomeric ions and

excess solubilizate is almost complete in this region and the break point may be taken as the C.M.C. for the micellar weight determinations.

The monomeric concentration Co decreases monotonically with an increase in the concentration of solubilizate. This is to be expected if one considers the incorporation of a hydrocarbon as effectively increasing the paraffin chain length of the H.T.A.B. molecule. Solubilization of a hydrocarbon therefore stabilizes the micelle to concentrations below its original C.M.C.. Using these Co values the $\frac{C-Co}{I-Io}$ versus (C-Co) curves are shown in graph(28). These curves deviate from linearity at low concentrations, presumably due to the proportion of molecularly dispersed molecules present. In the higher concentration region, however, good linearity of all the curves suggests that the micelles are of fixed composition in this region. As before the intercepts obtained by extrapolation of this linear relationship between $\frac{C-Co}{I-Io}$ and C-Co are subject to the errors involved in

HEXADECYL TRIMETHYL AMMONIUM BROMIDE + OCTANE

□ in water.

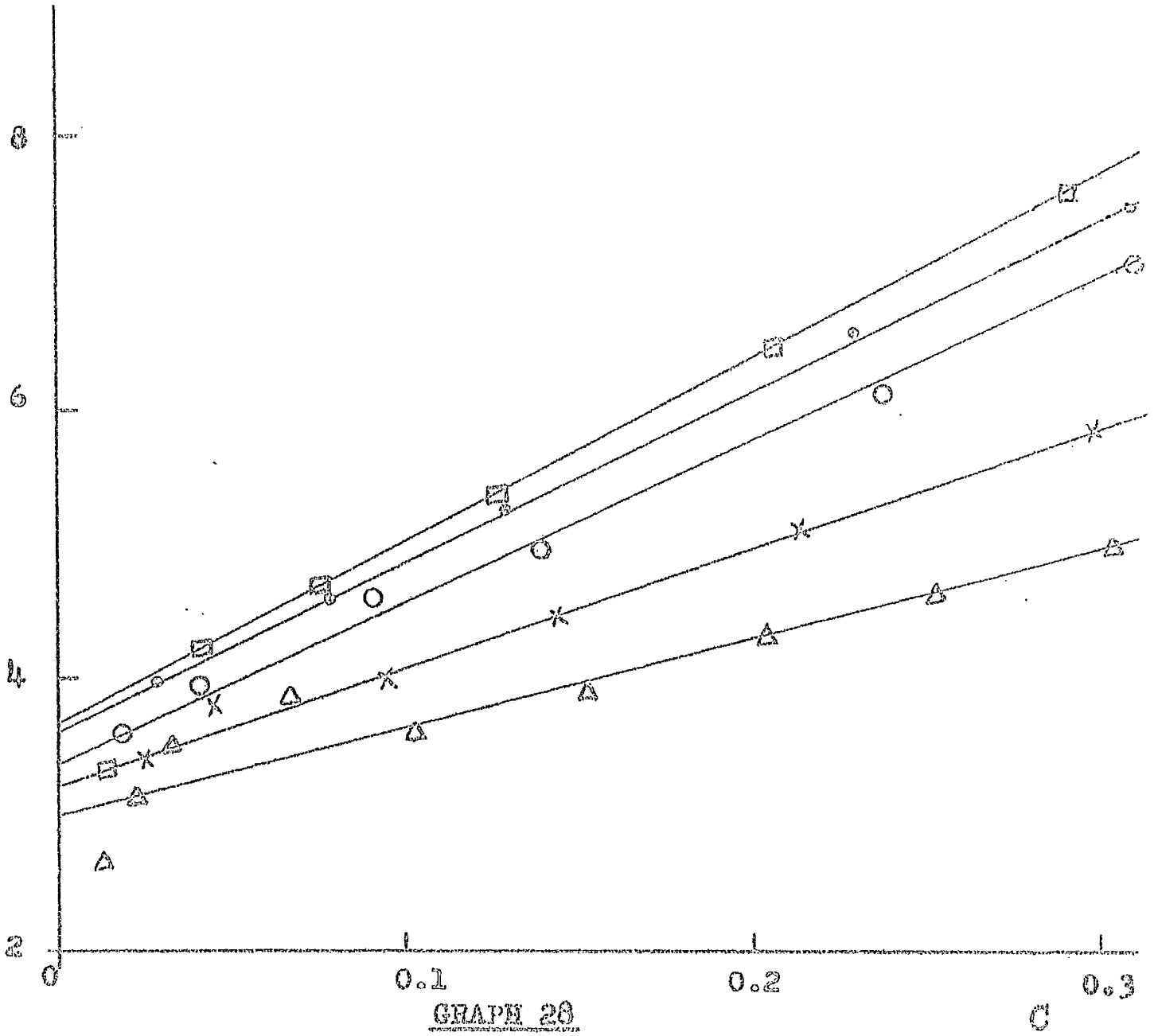
○ in 0.0198 gms. Octane.

○ in 0.033 gms. Octane.

× in 0.066 gms. Octane.

△ in 0.099 gms. Octane.

$\frac{C-C_0}{I-I_0}M.C.$



GRAPH 28

neglecting charge effects. Also the $\left(\frac{dn}{dc}\right)_C$ values, calculated from the interferometer readings, are presumably real although the variation in micellar weight recorded can scarcely leave the chemical potential constant and again calls in question the use of $\left(\frac{dn}{dc}\right)$ at constant concentration.

The results shown in table(7) are thus subject to some uncertainty which is difficult to eliminate but they give at least a qualitatively clear picture of the change in the constitution of micelles accompanying solubilization.

The following method was adopted for a calculation of the aggregation number of the micelle and the number of molecules of additive per micelle.

If n = the number of soap molecules per micelle.

M = the molecular weight of the additive.

x = concentration of additive in gms./100ml 1% H.T.A.B.

Co = C.M.C. in gms./100ml. soap.

and N = Avogadros Number.

Then, assuming the micelle to have the same constitution over

Solubilisate Octane	Amt. Hydrocarbon wt.% i.e. gm./100ml. 1% H.T.A.E.	Monomer Conc. Co x 10^2 gm/100 ml	Lim. $\frac{C-Co}{I-Io}$ x10^3	$\frac{dn}{dc}$	Apparent Micellar Weight	No. of Soap Molecules per micelle	No. of molecules octane/micelle
Density =0.70	0	7.8	3.7	0.143	26.100	72	0
$n^2$1.398	0.0198	7.2	3.6	0.143	26,900	72	5
M.W.114	0.033	6.2	3.4	0.144	28,000	74	8
M.V.163.3	0.066	5.6	3.22	0.145	29,200	75	17
	0.99	4.8	3.00	0.145	31,300	78	26

TABLE 7.

the concentration range Co to 1% such that the concentration of monomeric ions is Co over this range, we have:-

Micellar Weight = $364n$ + (Contribution from the additive).

The number of additive molecules in the system = $\frac{xN}{M}$

The number of micelles present = $\frac{(1-Co)N}{364n}$

Micellar Weight(M^*) = $364n + \frac{364n.xM}{(1-Co)N}$

$$M^* = 364n\left(1+\frac{x}{1-Co}\right)$$

and $$n = \frac{M^*(1-Co)}{364(1-Co+x)} \qquad \text{---------- (A)}$$

Also the number of additive molecules per micelle

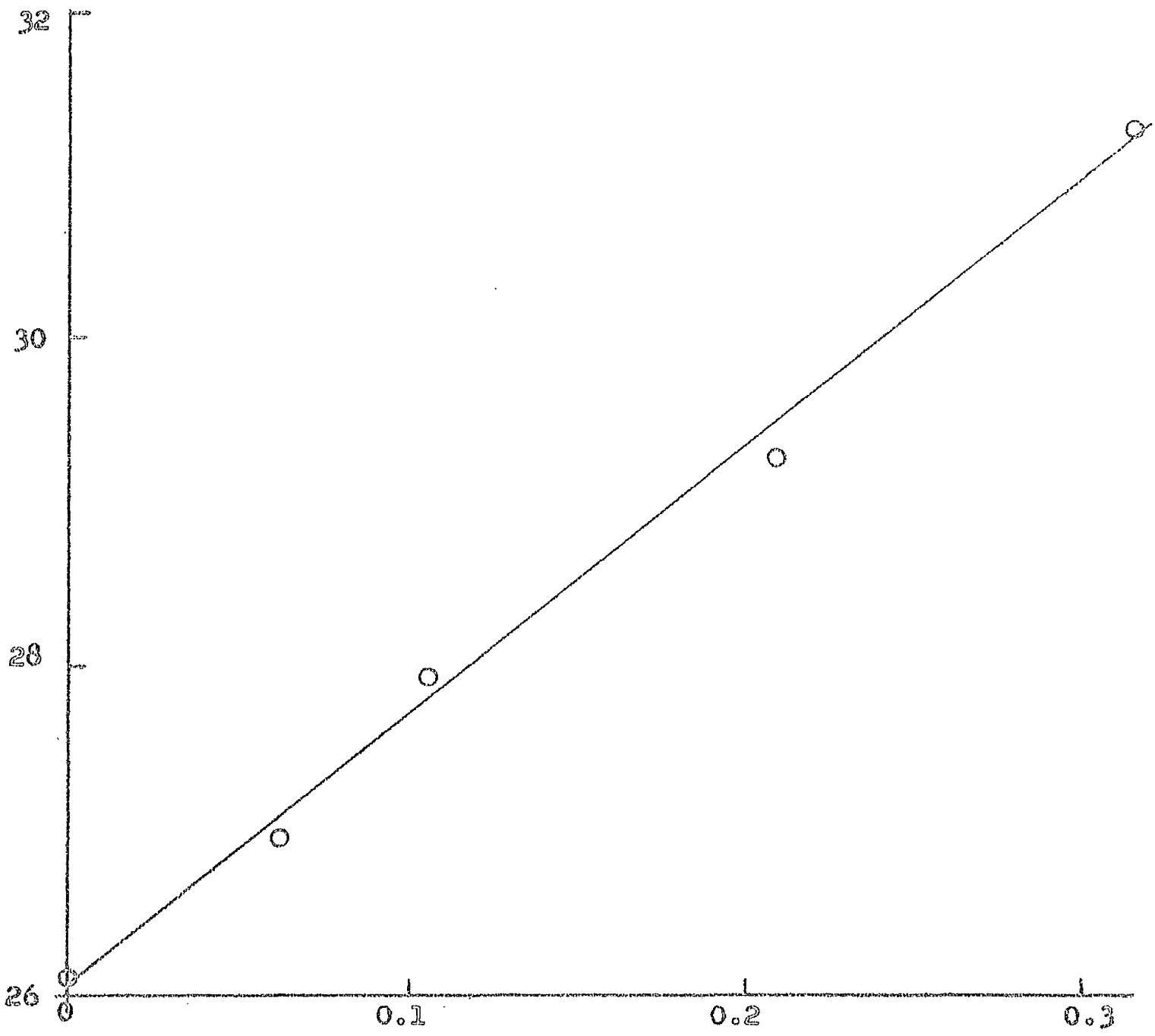
$$= \frac{A_o x_o 364}{(1-Co)M} \qquad \text{---------- (B)}$$

The concentration of monomeric soap decreases and the micellar weight increases with increasing amount of octane in all cases. This increase in micellar weight is accounted for not only by the incorporation of octane molecules in the paraffinic interior of the micelles but also by a change in

the number of detergent molecules per micelle. That is solubilisation appears to proceed with the reorganisation of the micelles. A plausible argument for the observed increase in micellar weight on the addition of octane is that by increasing the paraffinic content of the micelle interior it is effectively increasing the chain length of the soap. It is a well established fact that the higher homologues of a family of detergents have a much greater micellar weight. This also serves to illustrate that the micelle interior must have a configuration resembling that of a liquid.

In an effort to correlate the increase in micellar weight with the amount of octane solubilized, graph 29 was constructed. It can be seen that a linear relationship exists between the micellar weight and the molar ratio of octane to soap within the limits of experimental error. This relationship will no doubt hold until the saturation limit for solubilization is reached and is probably the best way of expressing the results.

HEXADECYL TRIMETHYL AMMONIUM BROMIDE + OCTANE.



GRAPH 29

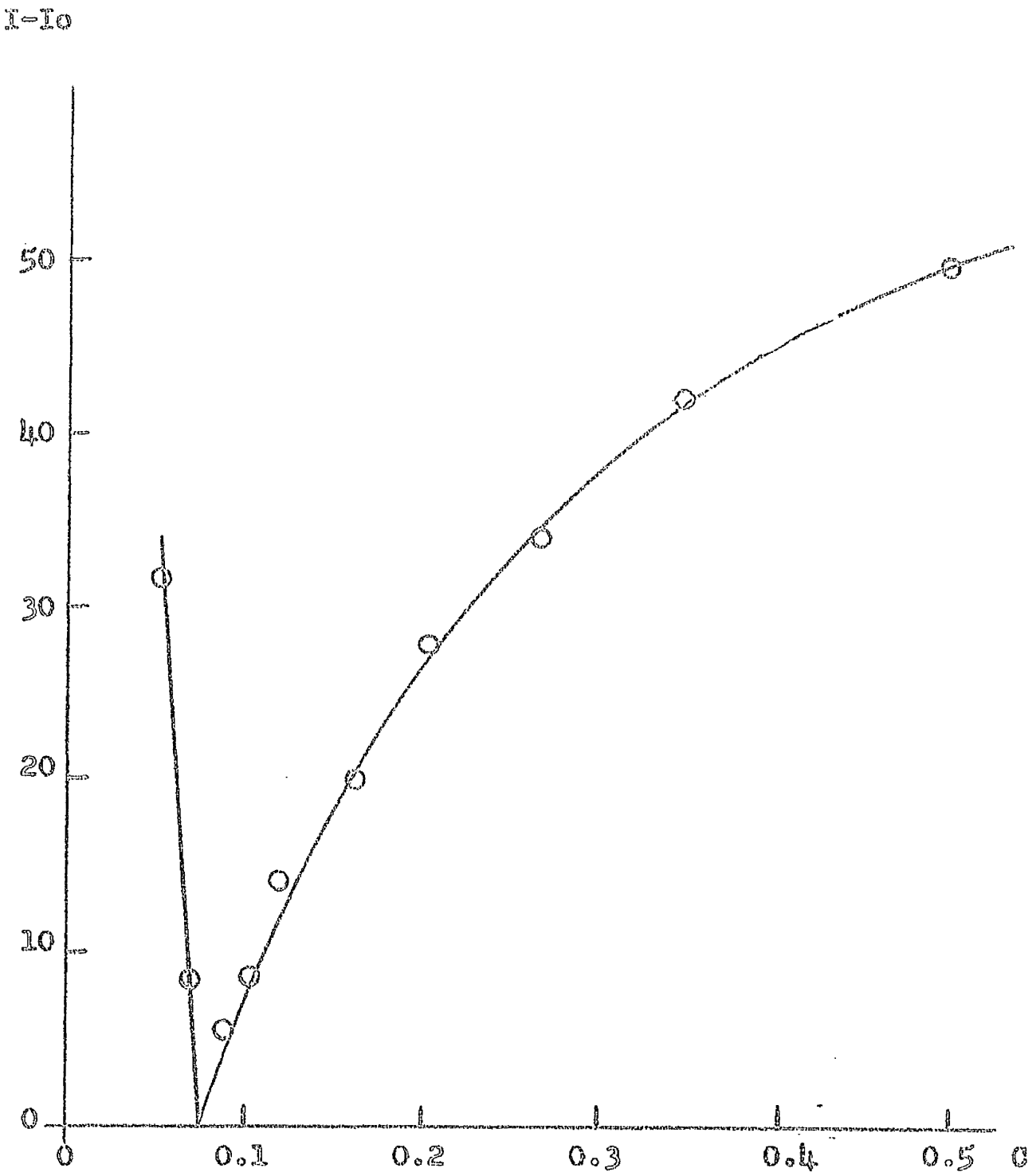
Addition of Decane:-

Experiments conducted with the higher paraffin decane as the solubilizate confirmed most of the findings with octane. Curves of I-Io versus C (graphs 30 A,B and C) illustrate the increase in scatter and respective lowering of the C.M.C. with increasing solubilizate concentration. Using the Co values obtained by extrapolation back to the C axis from these curves the plots of $\frac{C-Co}{I-Io}$ versus C-Co are shown in graph 31. As observed before these curves deviate from linearity at low concentrations but the intercepts obtained by extrapolation of the curves above (C-Co) = 0.1% back to zero concentration enable a calculation of the micellar weights. The $\left(\frac{dx}{de}\right)_C$ values are essentially constant over the concentration range measured, which is to be expected with a solubilizate of the same chemical composition as the micelle in which it is imbibed. The results are summarised in table 8 .

With respect to the weight of hydrocarbon added to the system the micellar weights recorded here are higher than those with octane. It must be remembered however that the molar volume of the former is 1.198 times that of the latter.

HEXADECYL TRIMETHYL AMMONIUM BROMIDE WITH DECANE

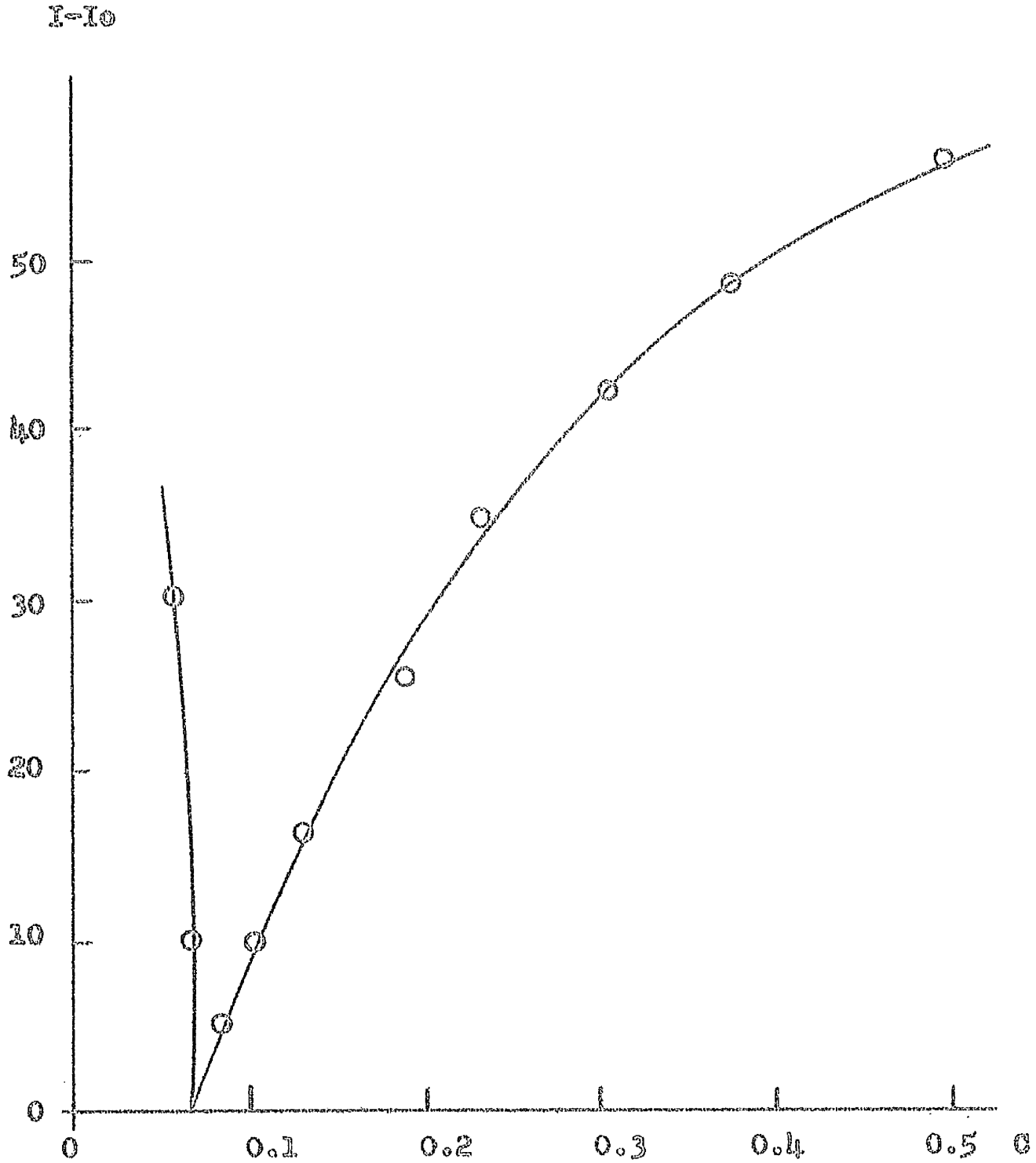
0.0136 gms/100 c.c.s. 1%



GRAPH 30A

HEXADECYL TRIMETHYL AMMONIUM BROMIDE WITH DECANE

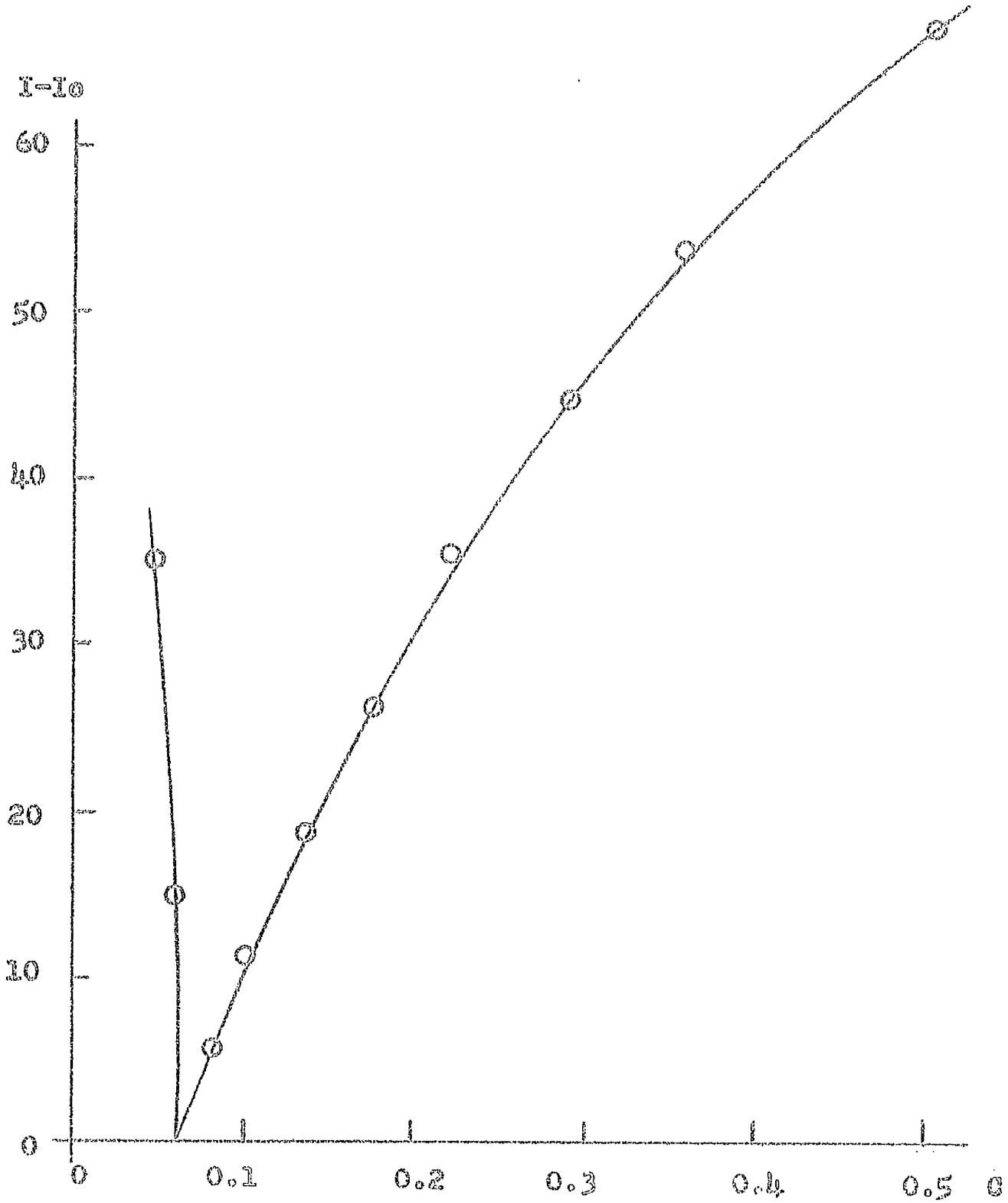
0.034 gms./100 c.c.s. 1%



GRAPH 30B

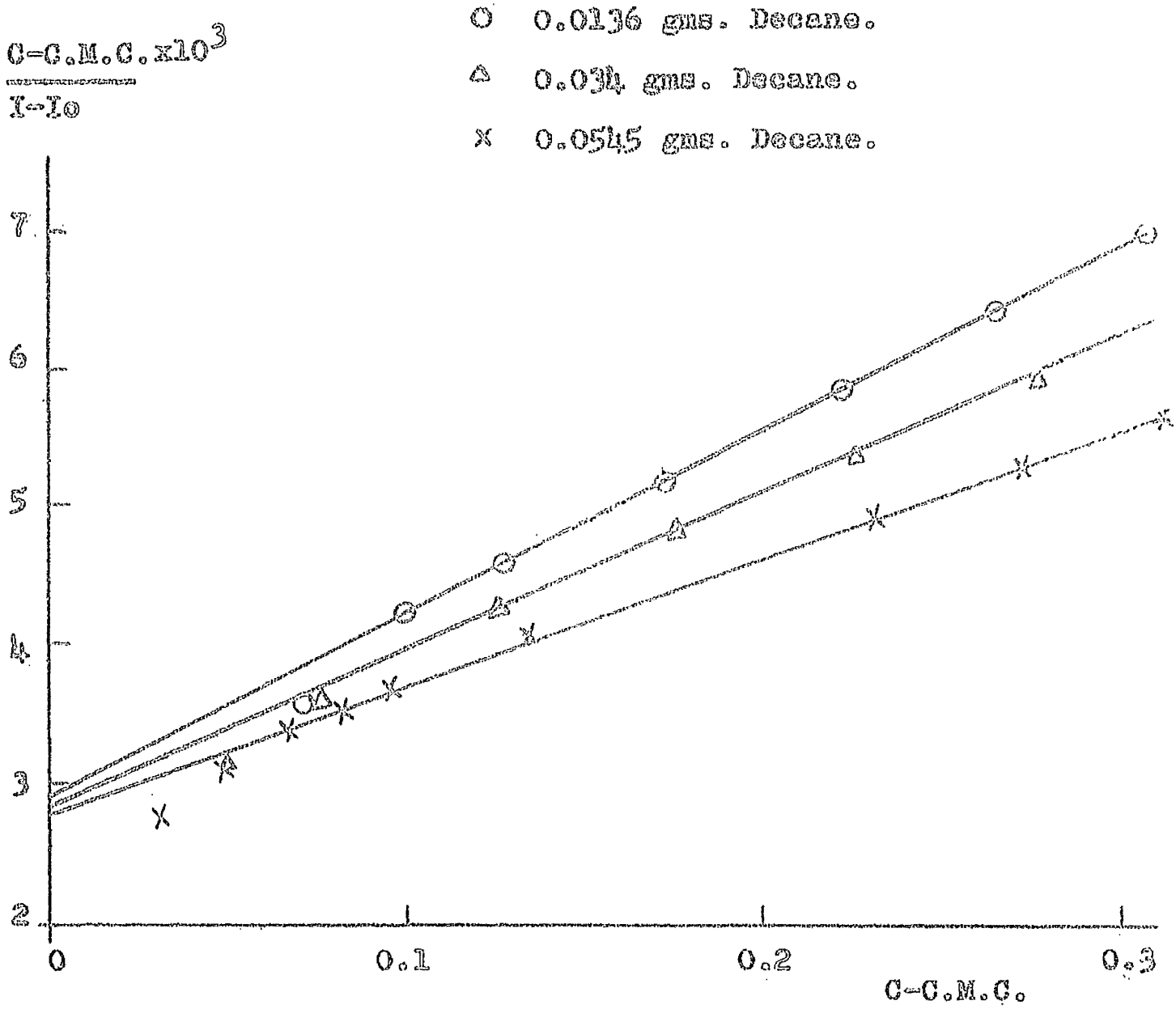
HEXADECYL TRIMETHYL AMMONIUM BROMIDE WITH DECANE

0.05h5 gms./100ml. 1%



GRAPH 30C

HEXADECYL TRIMETHYL AMMONIUM BROMIDE + DECANE.



GRAPH 31.

Solubilizate	Amt. Hydrocarbon gm./100ml. 1% K.T.A.B.	Monomer Conc. gm./100ml. $\times 10^{4}$	Lim. $\frac{C-C_0}{I-I_0}$ $\times 10^{3}$	$\frac{dn}{dc}$	Apparent Micellar Wt.	No. of Soap Molecules / Micelle	No. of decane molecules /micelle
Decane	0	7.8	3.7	0.143	26,100	72	0
Density 0.73	0.0136	7.8	2.91	0.147	31,400	85	2
n. =1.4120	0.034	7.5	2.85	0.148	32,100	85	6
M.W. = 142	0.0545	6.8	2.78	0.148	33,000	86	9
M.V. =196.1							

TABLE 8.

Indeed, comparing the two systems, the increase in micellar weight for the same weight of additive is roughly in this ratio.

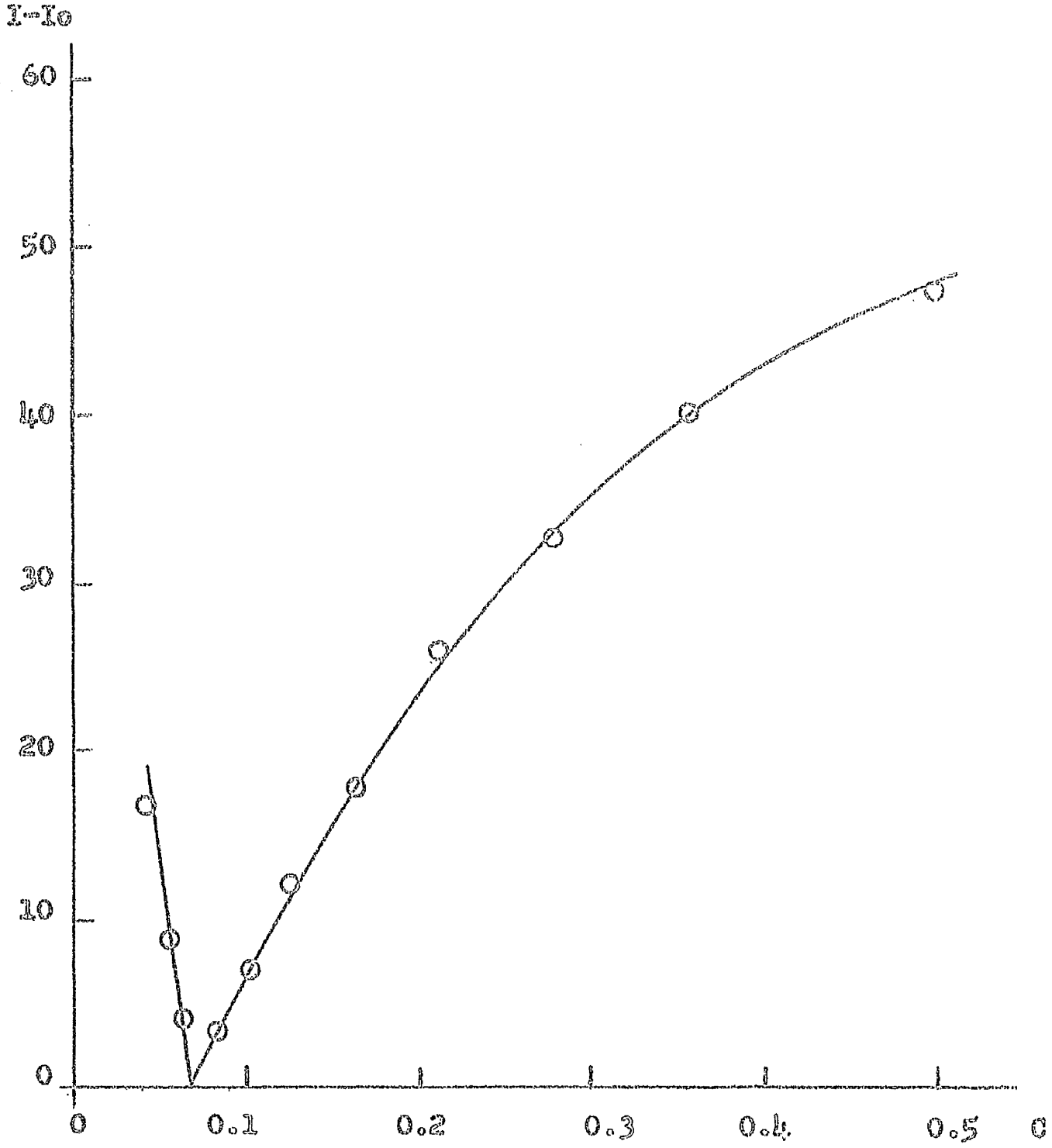
Addition of Cyclohexane:-

In order to compare the effect of the straight chain hydrocarbons on solubilization with a saturated cyclic hydrocarbon, a similar set of runs was conducted using cyclohexane as the solubilizate.

The curves of I-Io versus C (graphs 32A-D) are similar to those for the solubilization of the straight chain hydrocarbons, the scattering intensity increasing rapidly at a sharply defined point just below the C.M.C. for the pure soap. The curves of $\frac{C-Co}{I-Io}$ versus C-Co (graph 33) exhibit the same deviation from linearity at low concentrations though sufficient points lie on a straight line to enable the $\frac{C-Co}{I-Io}$ value at infinite dilution to be determined. At the higher cyclohexane concentrations $\left(\frac{dn}{dc}\right)$ tends to increase from the original soap value. n^D for cyclohexane is 1.429 which is higher than the two hydrocarbons already investigated. The results are summarised in table 9.

NEXADECYL TRIMETHYL AMMONIUM BROMIDE WITH CYCLOHEXANE

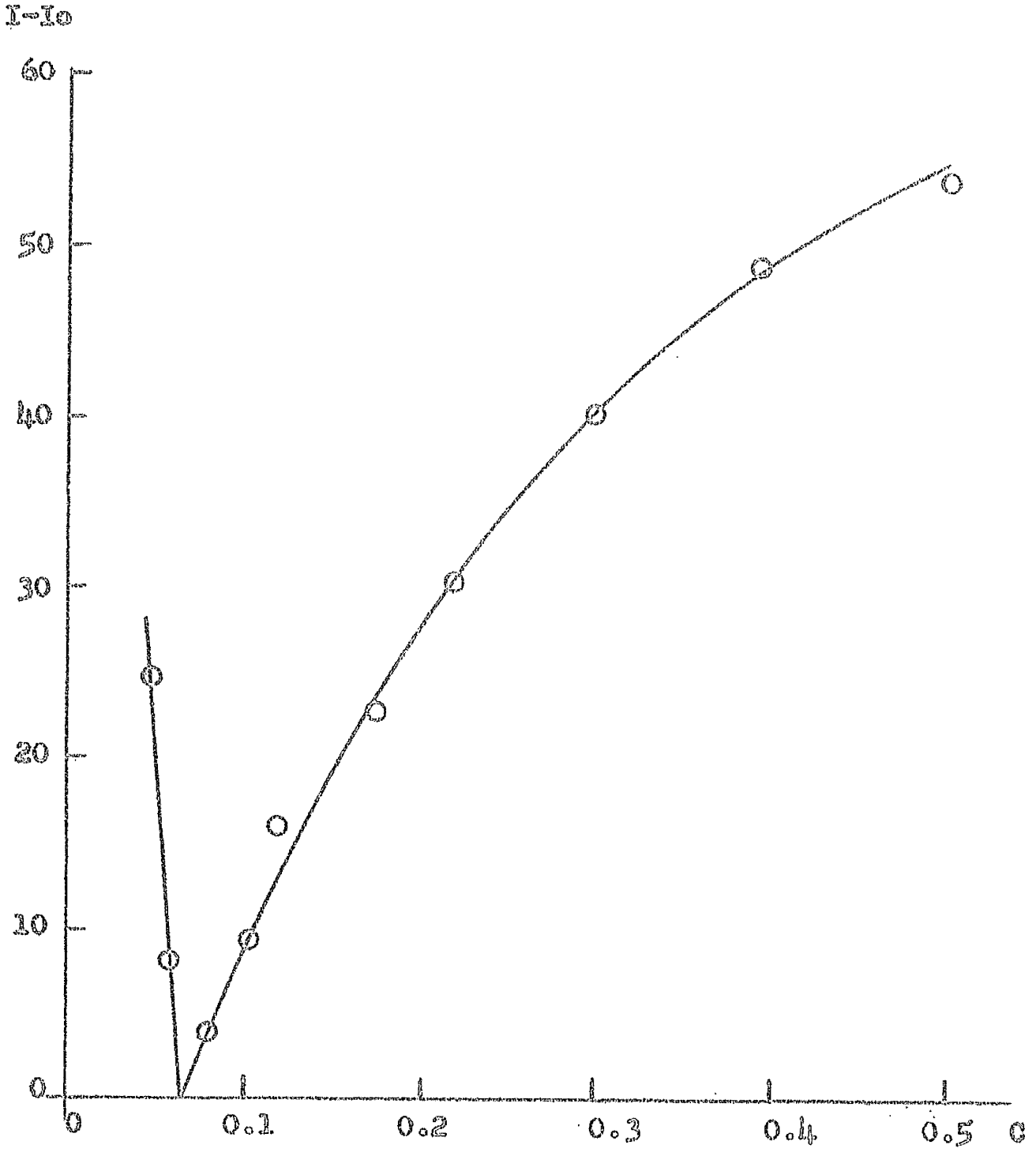
0.021 gms/100 ml. 1%



GRAPH 32A

HEXADECYL THIMETHYL AMMONIUM BROMIDE WITH CYCLOHEXANE

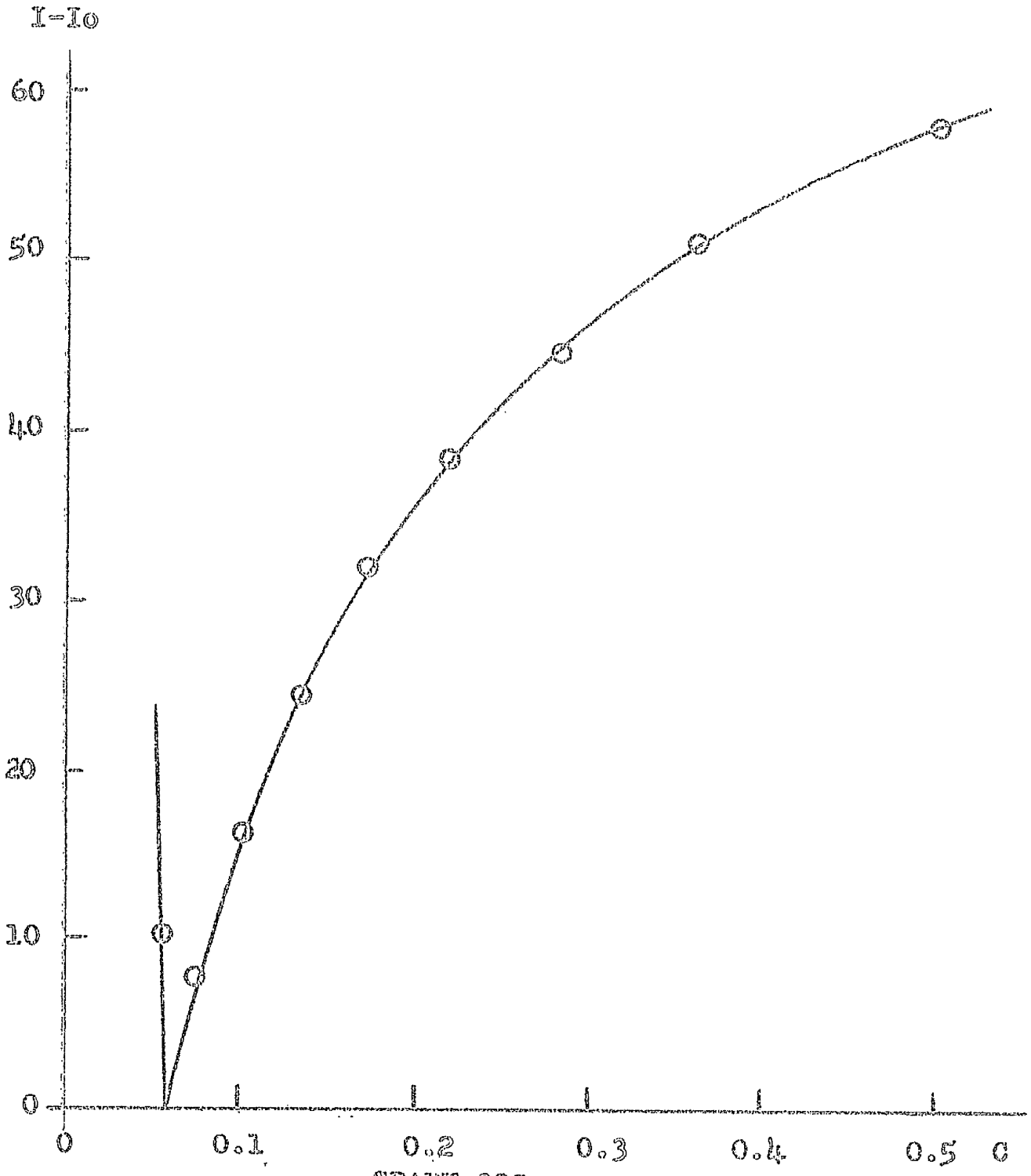
0.034 gms/100ml 1%



GRAPH 32B

HEXADECYL TRIMETHYL AMMONIUM BROMIDE WITH CYCLOHEXANE

0.1001 gms/100 ml. 1%

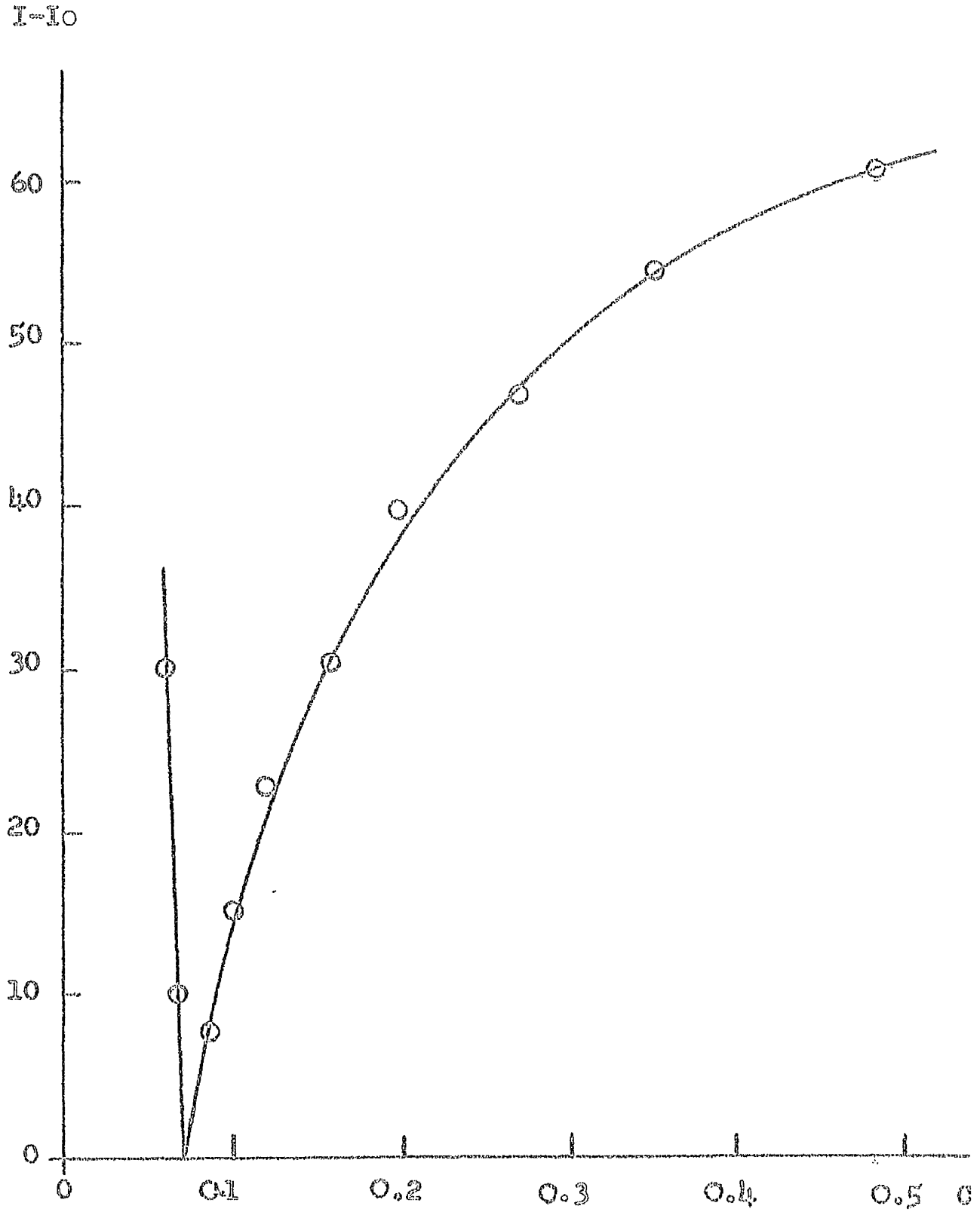


GRAPH 32C

HEXADECYL TRIMETHYL AMMONIUM BROMIDE WITH CYCLOHEXANE

HEXADECYL TRIMETHYL AMMONIUM BROMIDE WITH CYCLOHEXANE

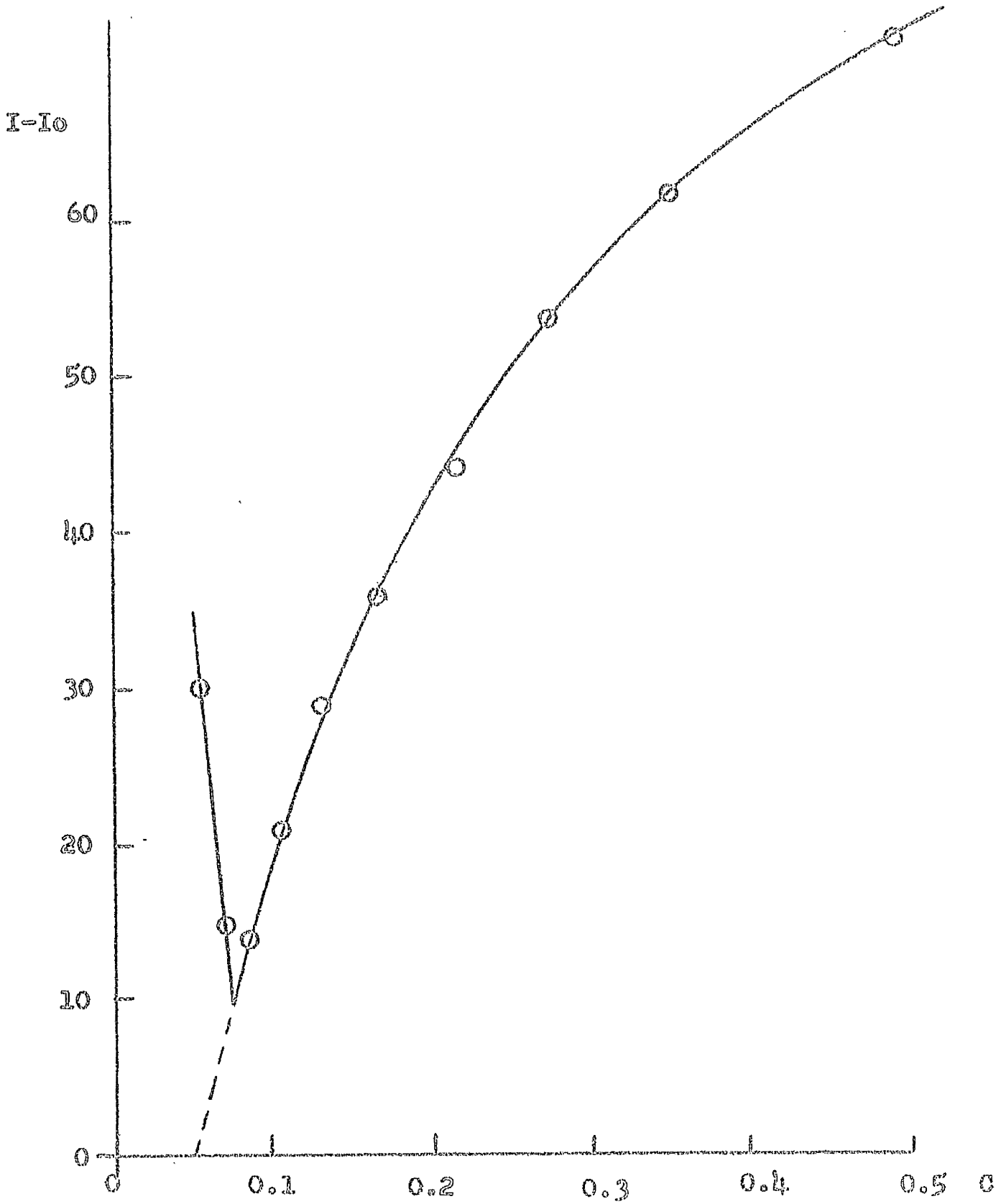
0.134 gms/100ml 1%



GRAPH 32D

HEXADECYL TRIMETHYL AMMONIUM BROMIDE WITH CYCLOHEXANE

0.1675gms/100ml 1%



GRAPH 32E

HEXADECYL TRIMETHYL AMMONIUM BROMIDE + CYCLOHEXANE

○ 0.021 gms. cyclohexane

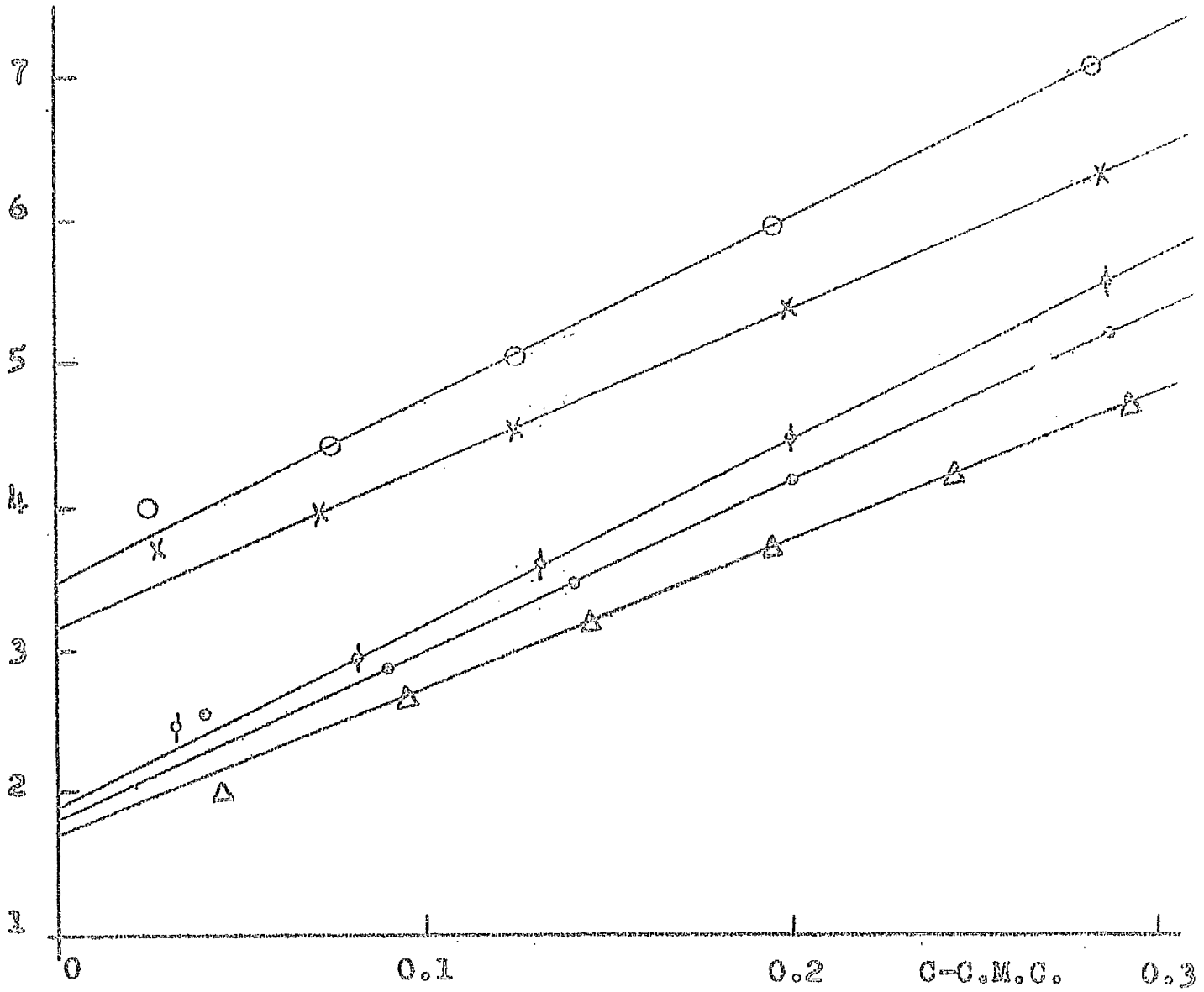
× 0.034 gms. cyclohexane

◊ 0.1001 gms. cyclohexane.

∘ 0.134 gms. cyclohexane.

△ 0.1675 gms. cyclohexane.

$\frac{C-C.M.C.}{I-Io} \times 10^3$



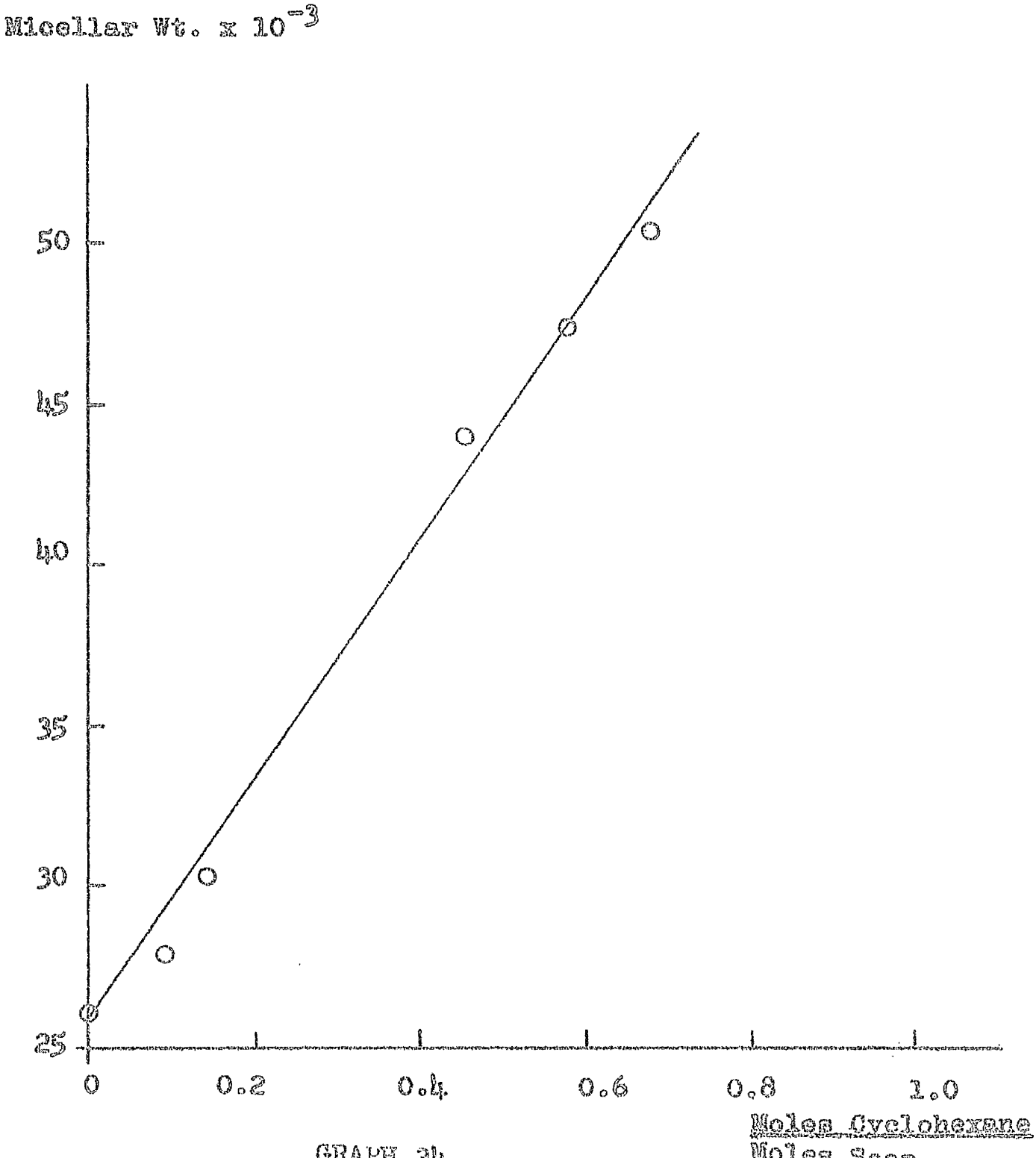
GRAPH 33.

Solubilizate	Amt. Hydrocarbon gms./100ml. 1% H.T.A.B.	Monomer Conc. gms./100ml. $\times 10^2$	Lim. $\frac{C-Ce}{I-Ic}$ $\times 10^3$	$\left(\frac{dn}{dc}\right)$	Apparent Micellar Weight	No. of Soap Molecules /micelle.	No. of cyclohexane molecules /micelle.
Cyclohexane Density 0.78 n = 1.429 M.W. 84 M.V. 104.5	0	7.8	3.7	0.143	26,100	72	0
	0.021	7.6	3.48	0.144	27,400	74	7
	0.034	7.4	3.15	0.147	29,800	79	13
	0.1001	6.8	1.90	0.153	44,500	110	51
	0.134	6.0	1.80	0.152	47.400	114	70
	0.1675	5.6	1.70	0.153	49,800	116	89

TABLE 9.

As with octane and decane the general feature of a reconstitution of the micelle accompanying the increase in micellar weight with increasing amounts of additive was evident. One can also conclude that there is approximately a direct proportion between the micellar weight and the molar ratio of additive to soap.(graph 34). There is little difference between the results obtained for cyclohexane and the straight chain hydrocarbons, signifying that the same solubilization mechanism is invoked. The higher solubilization limit with the cyclic hydrocarbon can be attributed to its more compact chemical configuration. Some evidence can be found here for the suggestion that there is a certain void space within the micelles. It will be noted that small additions of cyclohexane, indeed up to 7 molecules per micelle, makes little or no impression on the aggregation number of the micelle. This suggests that there is very little enlargement up to that point. However, subsequent addition of solubilizate leads to a measureable reconstitution and growth of the micelle. Thus it seems

HEXADECYL TRIMETHYL AMMONIUM BROMIDE + CYCLOHEXANE



GRAPH 34

probable that up to a certain point, governed by the amount of space in the micelle interior available to the solubilized material, any increase in micellar weight is due to the incorporation of additive within the micelle and after that to the solubilized material and the reconstitution of the micelles caused by it.

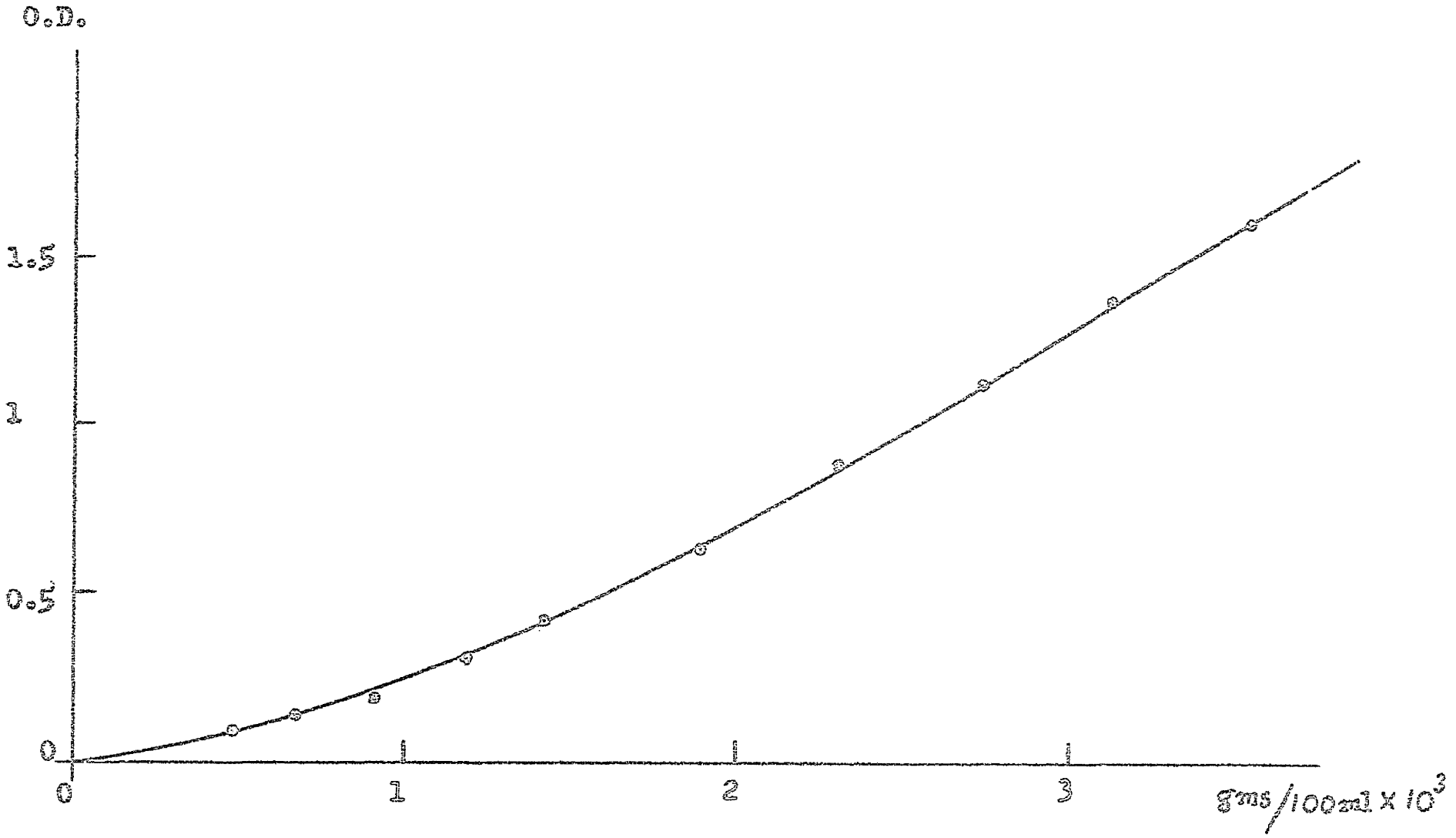
Addition of Benzene:-

With benzene as the solubilisate one can no longer conveniently assume that the solubility of the additive in water is zero. By means of optical density measurements on a Unicam spectrophotometer (at 200 mμ.) the solubility of benzene in water was found to be 0.17gms./100 ml. at 25°C, which is precisely the value obtained by Franks and Gent(106). In order to obtain an estimate of the distribution of benzene between micelles and water in an H.T.A.B. solution, a model solution was constructed treating the micelles as a separate phase. Adding 0.678 gms. of decane to 100 c.c.s. of water produces an inhomogeneous mixture of the same paraffinic content as the 1% H.T.A.B. solution. In principle the hydrocarbon should

be mixed with a dilute solution of an electrolyte of the same potential as the soap solution but it was found experimentally thatsmall additions of KBr did not affect the final result. The same weights of benzene as those employed in the solubilization experiments were added to the paraffin-water mixtures and after thoroughly mixing the three component system for 24 hours a sample of the water layer was removed and its optical density measured on the Unicam spectrophotometer. The benzene content of the water is obtained directly from the calibration curve of O.D. versus benzene concentration (graph 35). The benzene dissolved by the paraffin is of course obtained by subtracting the amount in the water from the total added.

The calibration experiments confirmed the findings of Arnold et.al. (109) that aqueous solutions of benzene at low benzene concentration do not obey Beers Law. The results from these partition experiments are shown in Table 10.

CALIBRATION OF OPTICAL DENSITY V'S BENZENE IN WATER



GRAPH 35

TABLE 10.

Wt.of Benzene Added to 100ml. mixture	Wt.Benzene in Water Calculated	Wt. in Paraffin	$K = \frac{\text{Wt. Benzene in Paraffin}}{\text{Wt. Benzene in Water}}$
0.0365	0.0038	0.0327	8.6
0.073	0.0136	0.0594	4.36
0.110	0.0254	0.0846	3.33
0.147	0.0481	0.0989	2.05
0.22	0.0721	0.1479	2.04

It appears from this experiment that distribution is very much in favour of the paraffin at low benzene concentrations but that this is altered at higher benzene content to just over double the amount in the paraffin as compared with the aqueous layer. The partition coefficient may be lowered still further with benzene concentrations approaching the solubilization limit of 0.485 grams. If the aqueous layer is also fully saturated at this point K would be 1.84. Although this model is a very crude representation of a homogeneous micellar solution, in which the paraffin is evenly distributed throughout the water,

it seems the only convenient way that these partition coefficients can be evaluated . The total amounts of solubilizate added were therefore altered accordingly in the final analysis.

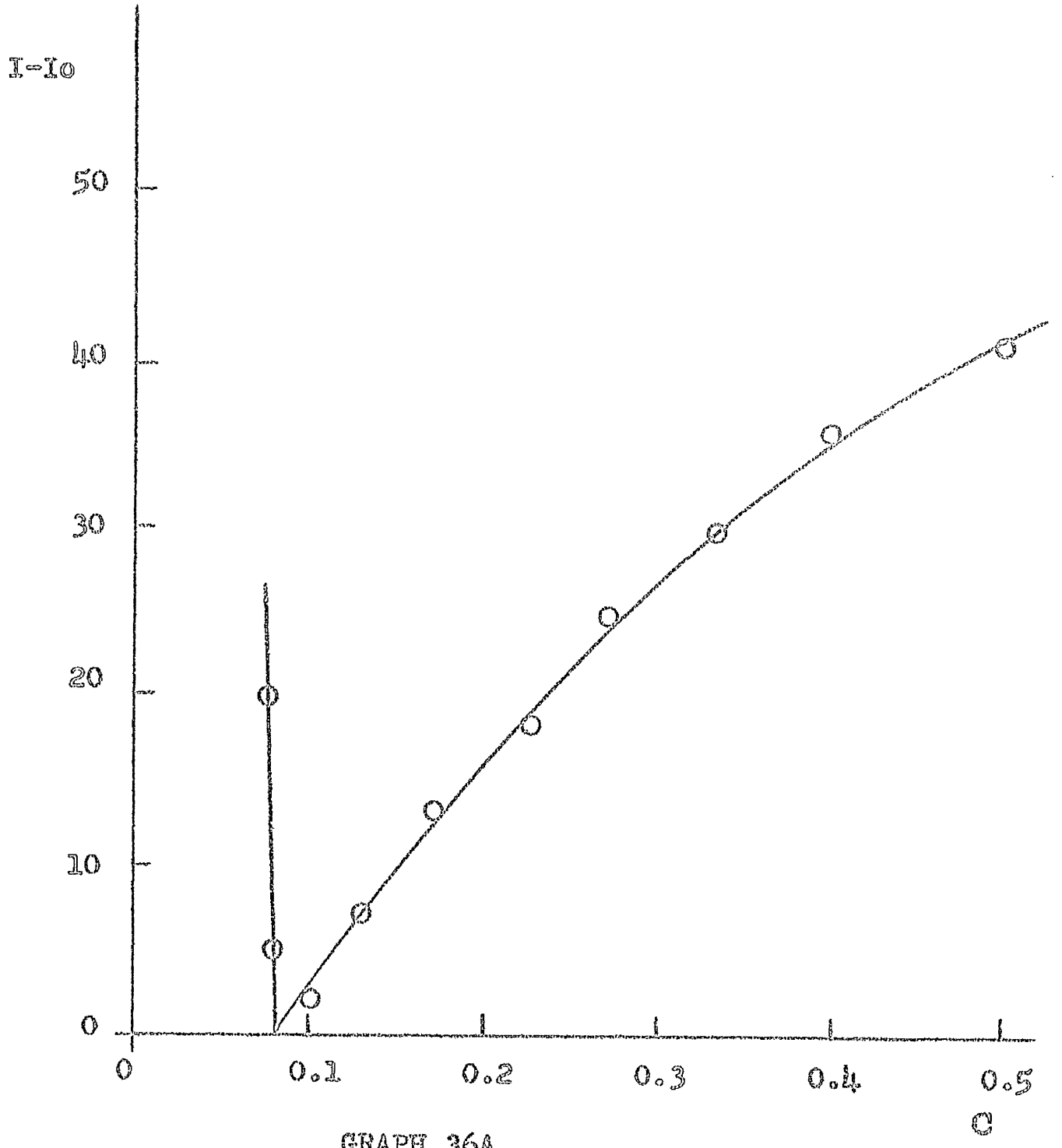
The results from light scattering by the solubilized benzene solutions (graphs 36 A-D and 37) were computed in the same way as with the other solubilized systems. The final analysis is given in table II. An allowance was made for the scatter from aqueous benzene rather than pure water, the concentration of benzene being based on the partition coefficient experiments.

The apparent lowering of the micellar weight with small additions of benzene, up to about 0.12 grams/100ml. 1% H.T.A.B., is a peculiarity not exhibit by the other solubilizates. A possible explanation might be that due to its polarisability benzene is first located at the micellar surface, thus forcing an attenuated micellar reconstitution. At higher concentrations this locus will spread to the micelle interior leading to the recorded increase. Due to its high affinity for paraffins one

TABLE 11 Benzene - as Additive

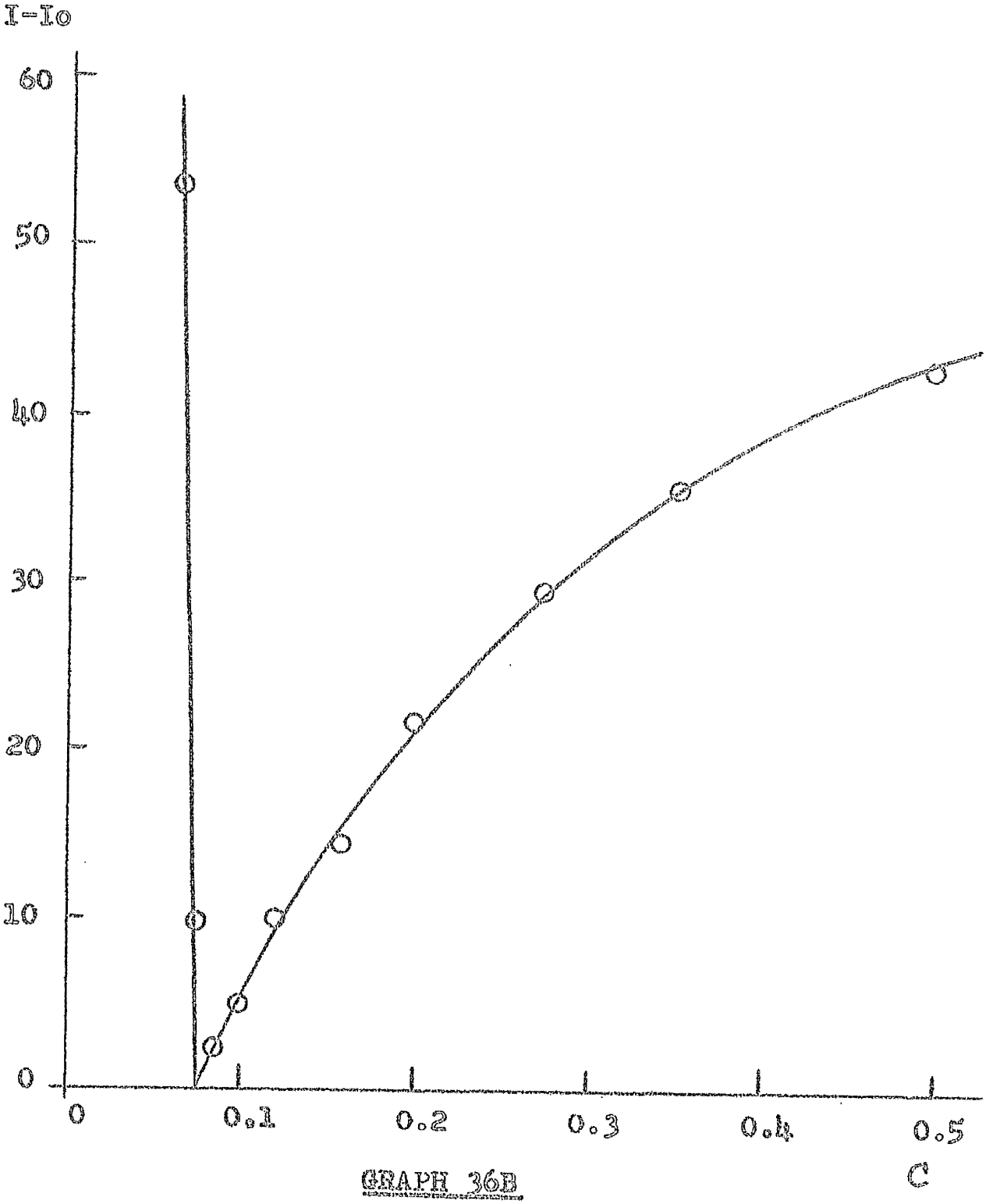
Amt. Added wt.% 1 CTAB gm./100 ml.	Amt. in Micelle Calc.	Monomer Conc. Co x 10^2 gm/100 ml.	Lim. $\frac{C-MC}{V}$ x 10^5	$\frac{da}{dc}$	Micellar wt.	No. of Soap Molecules per micelle	No. of Oil Molecules/ Micelle
0	0	7.8	3.7	0.143	26,100	72	0
0.073	0.0594	9.2	4.85	0.147	19,900	52	15
0.11	0.0846	8.0	3.96	0.148	25,200	60	26
0.147	0.0989	7.4	2.51	0.154	33,200	85	42
0.22	0.1479	6.0	1.47	0.171	45,800	112	82

H.T.A.B. WITH BENZENE 0.073gms/100 ml. 1%



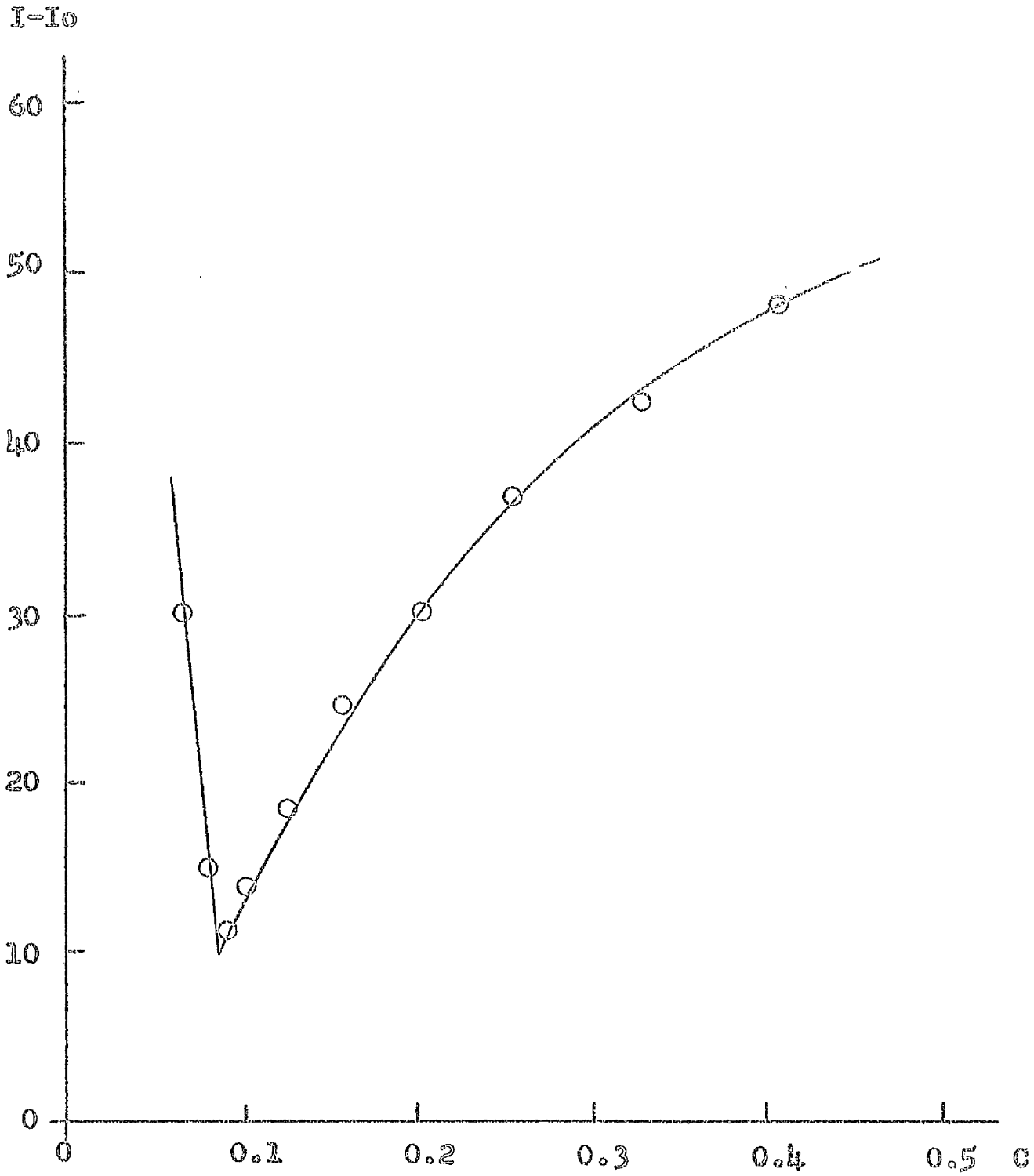
GRAPH 36A

H.T.A.B. WITH BENZENE 0.11 gms./100 ml. 1%



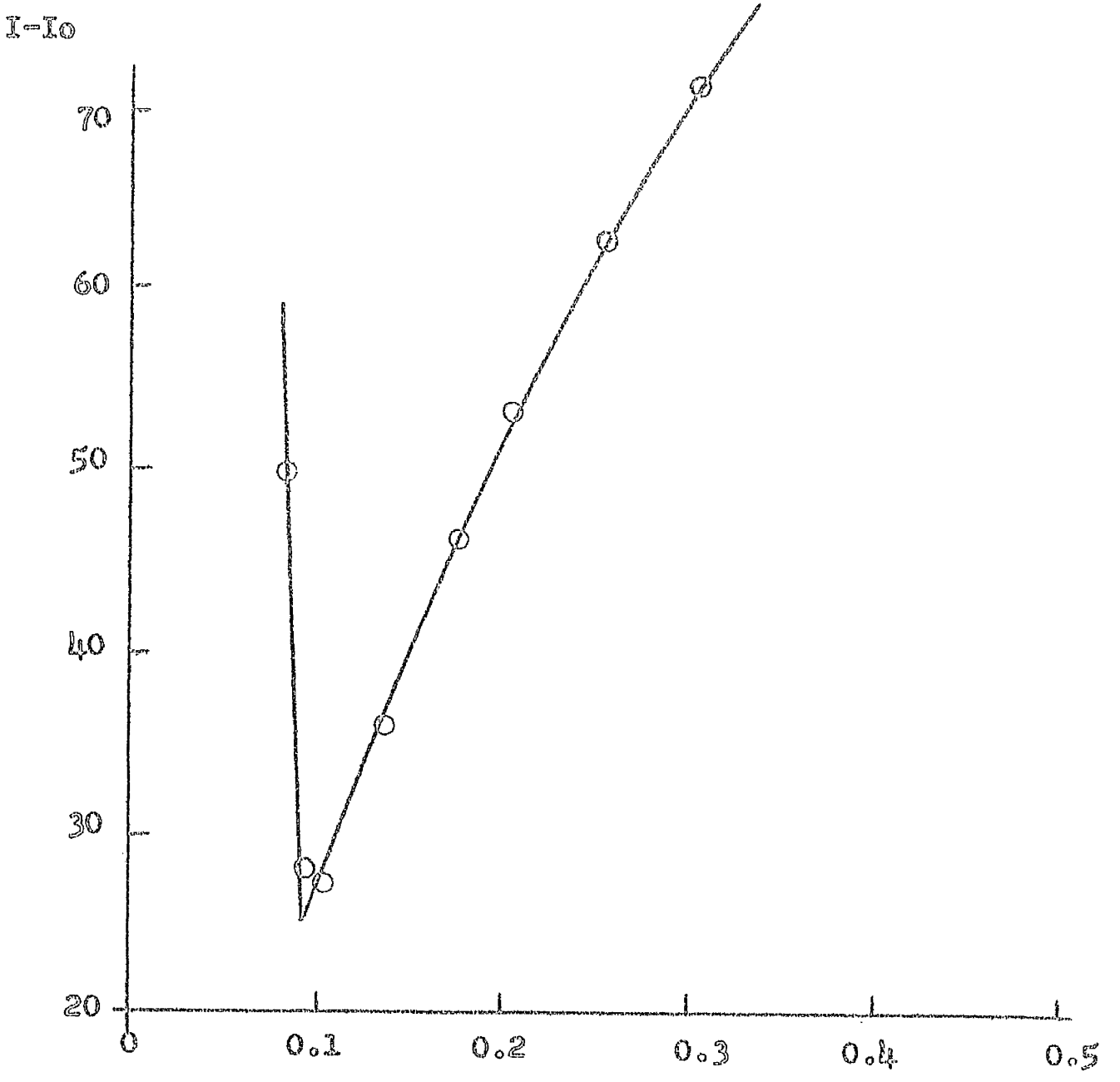
GRAPH 36B

H.T.A.B. WITH BENZENE 0.147 gms/100ml. 1%



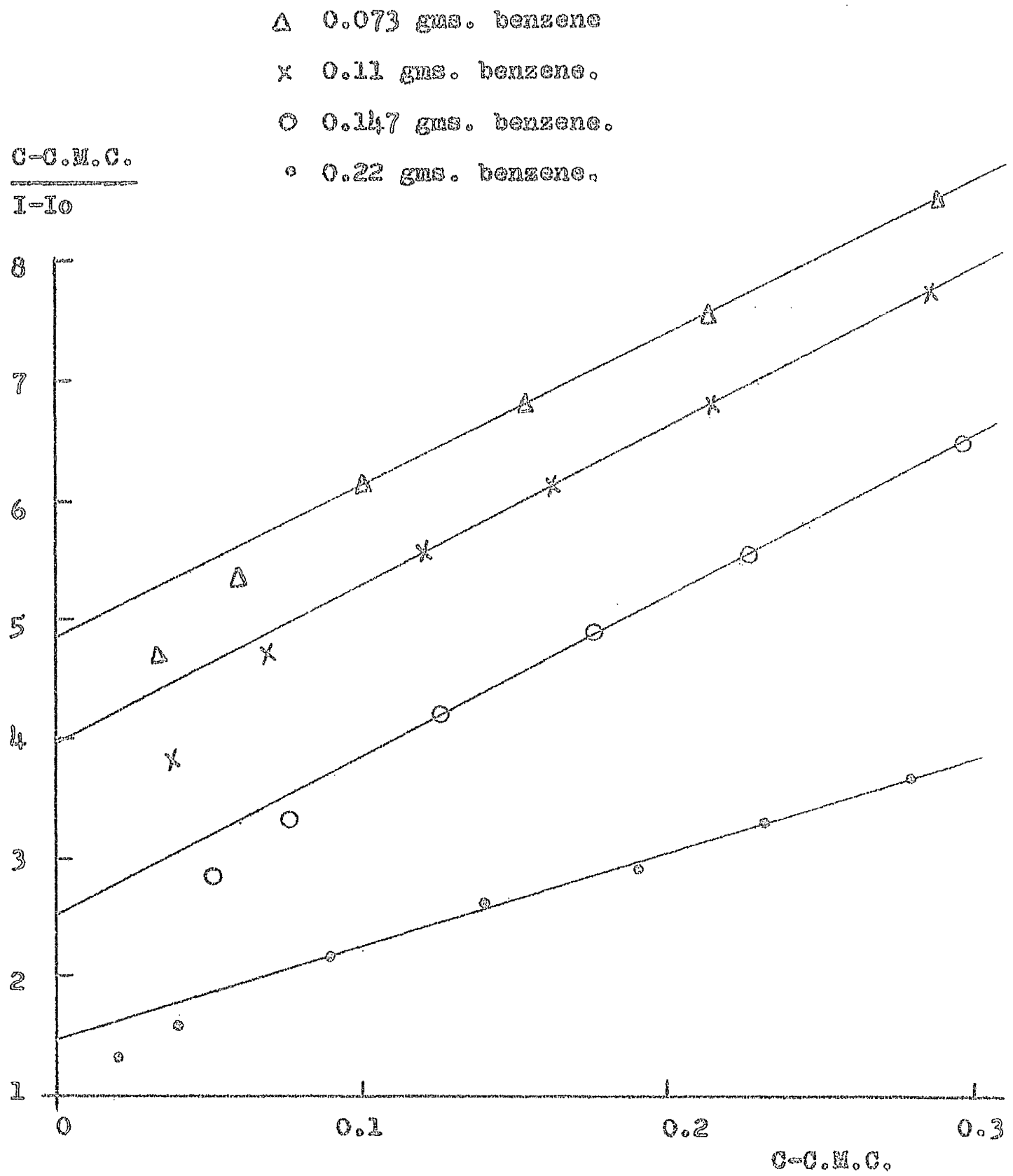
GRAPH 36C

N.T.A.B. + BENZENE 0.22 gms./100 ml. 1%



GRAPH 36D

HEXADECYL TRIMETHYL AMMONIUM BROMIDE + BENZENE



GRAPH 37

would expect the reverse to be true. Hyde and Lawrence(107) have reported that the conductivity of solutions of H.T.A.B. (1.5%) falls with small additions of benzene up to about 0.25 gms./10ml. H.T.A.B. then increases, passing through a maximum, before decreasing once again. The benzene solution over the range where the conductivity exhibits a maximum was viscoelastic. These measurements were done at much higher benzene concentration than those studied here, though it is clear that the solubilization mechanism with benzene as solubilizate is much more complicated than that of the other additives. The observed minimum in Λ is however within the limits of the amounts of benzene used in this study and could be accounted for by the dual mechanism suggested above. [It is worth noting that the calculations are based on a rather naïve model. The benzene distribution between micelle and water as calculated here may be subject to considerable error thus accounting for the anomalous behaviour.]

Octanol and Decanol as Solubilizates:-

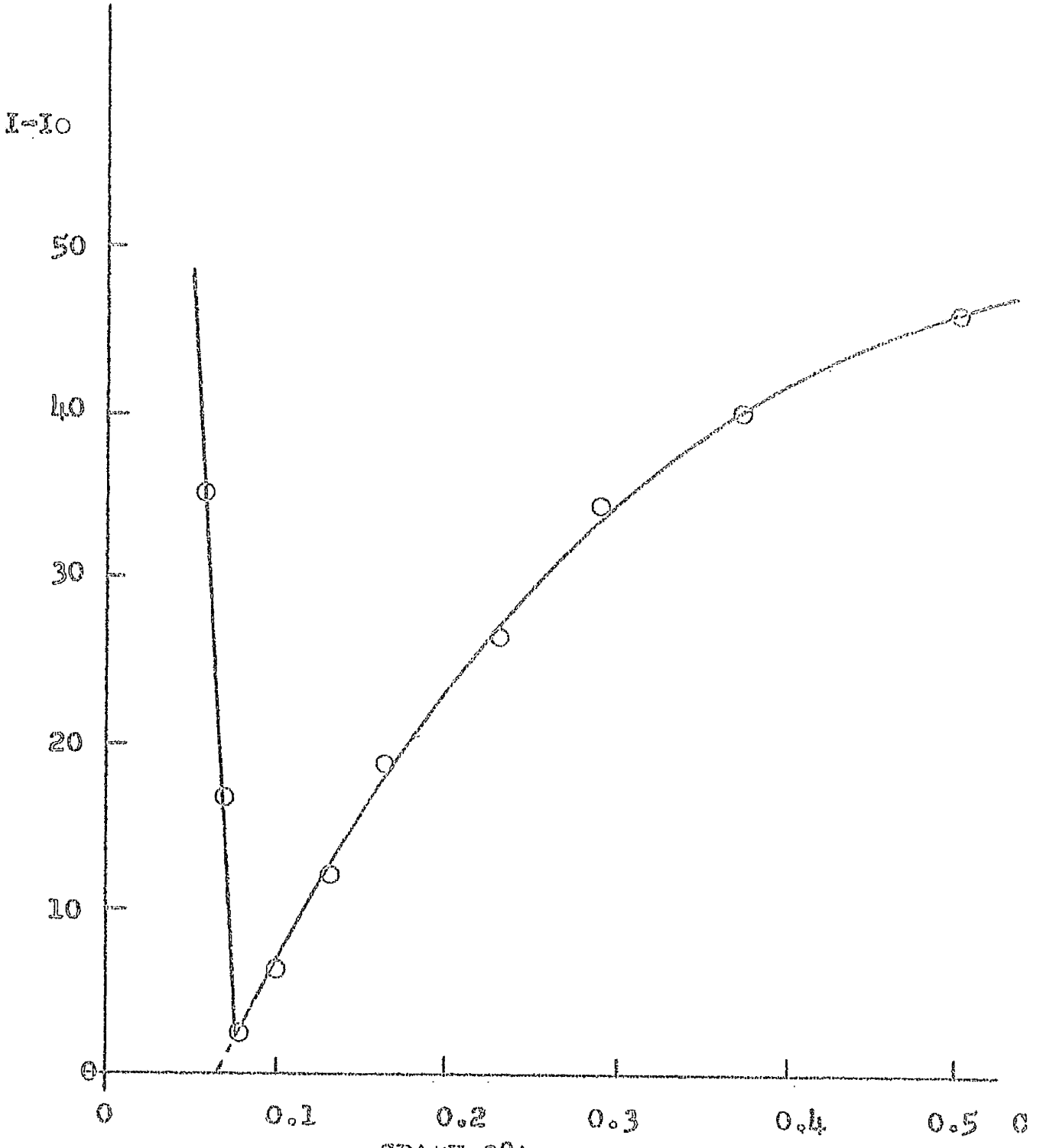
Unfortunately dilute solutions of H.T.A.B. (still above the C.M.C.) containing small amounts of octanol and

decanol, well below the visual saturation limit, still contain undissolved alcohol at 25°C. The light beam passing through these solutions displays much 'sparkle' when observed through a periscope mounted on the machine. This 'sparkle' which is much more pronounced with decanol than octanol, can be eliminated by increasing the temperature of the solutions (graphs 38 A-D). The increase in temperature presumably renders the small amount of unsolubilized alcohol, water soluble. An increase in temperature to 35°C has no effect on the light scattered by the pure soap so that micellar weights can be estimated at this temperature for small additions of alcohol.

For small additions of octanol the following results (Table 12) have been obtained at 35°C in the usual manner from graphs 38 and 39.

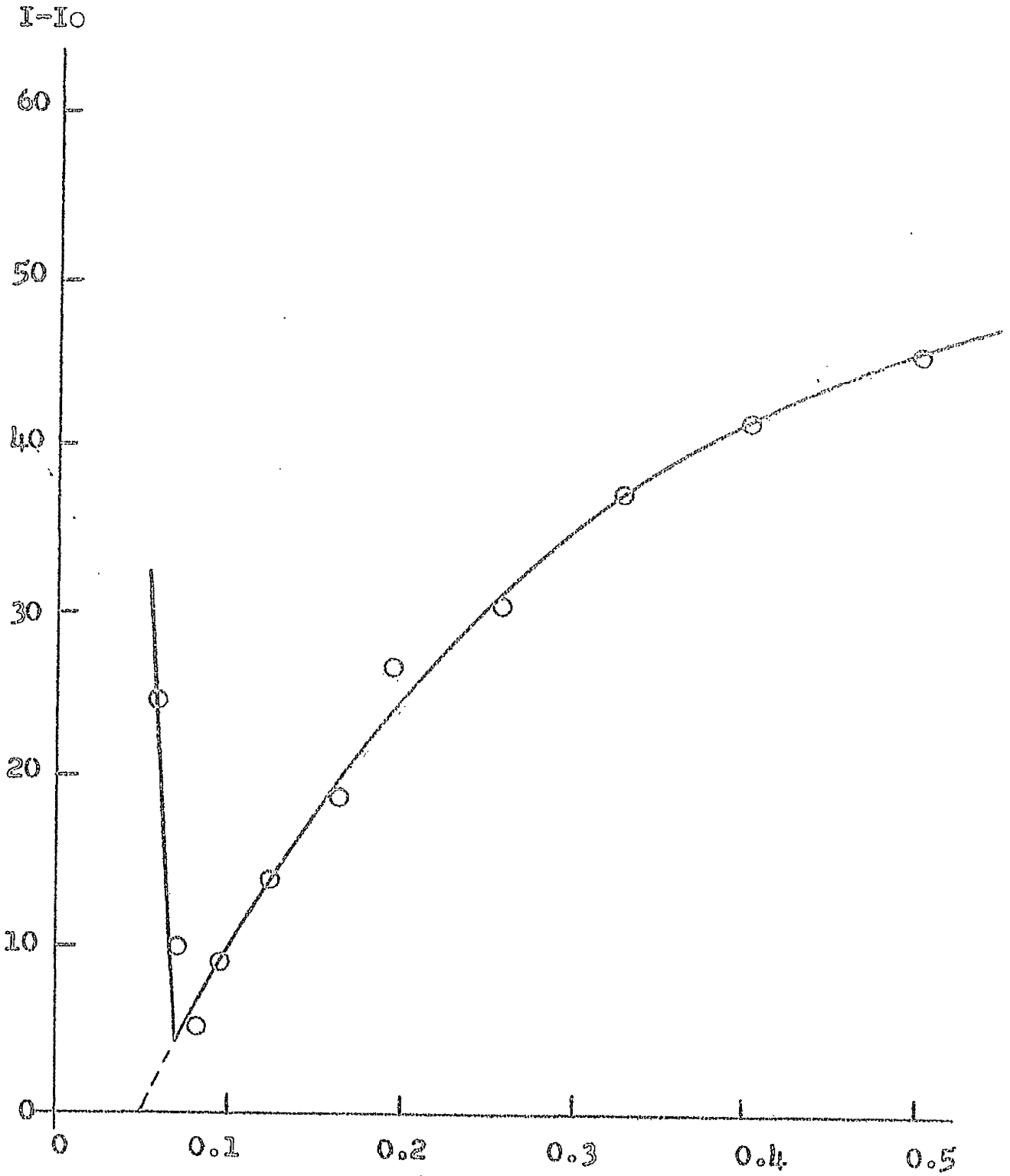
From the above analysis it is clear that there is a pronounced difference between the penetration type of solubilization into the palisade layer, manifested by the long chain alcohols, and the incroporation of solubilizate in the micelle interior as with hydrocarbons. In the former case

H.T.A.B. + OCTANOL 0.0495 gms./ 100 ml. at 35°C



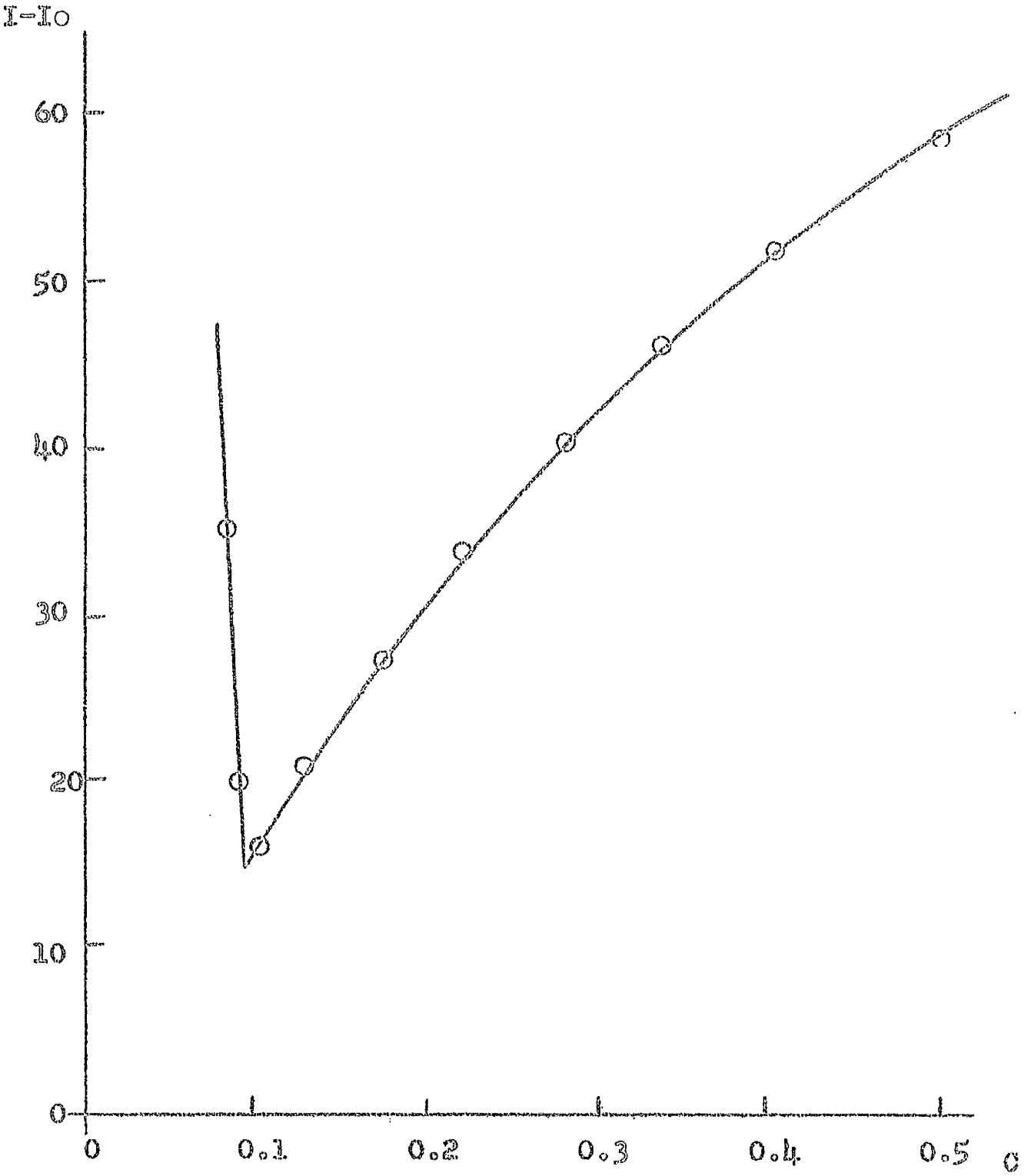
GRAPH 30A

H.T.A.B. + OCTANOL 0.099 gms./100 ml 1% at 35°C



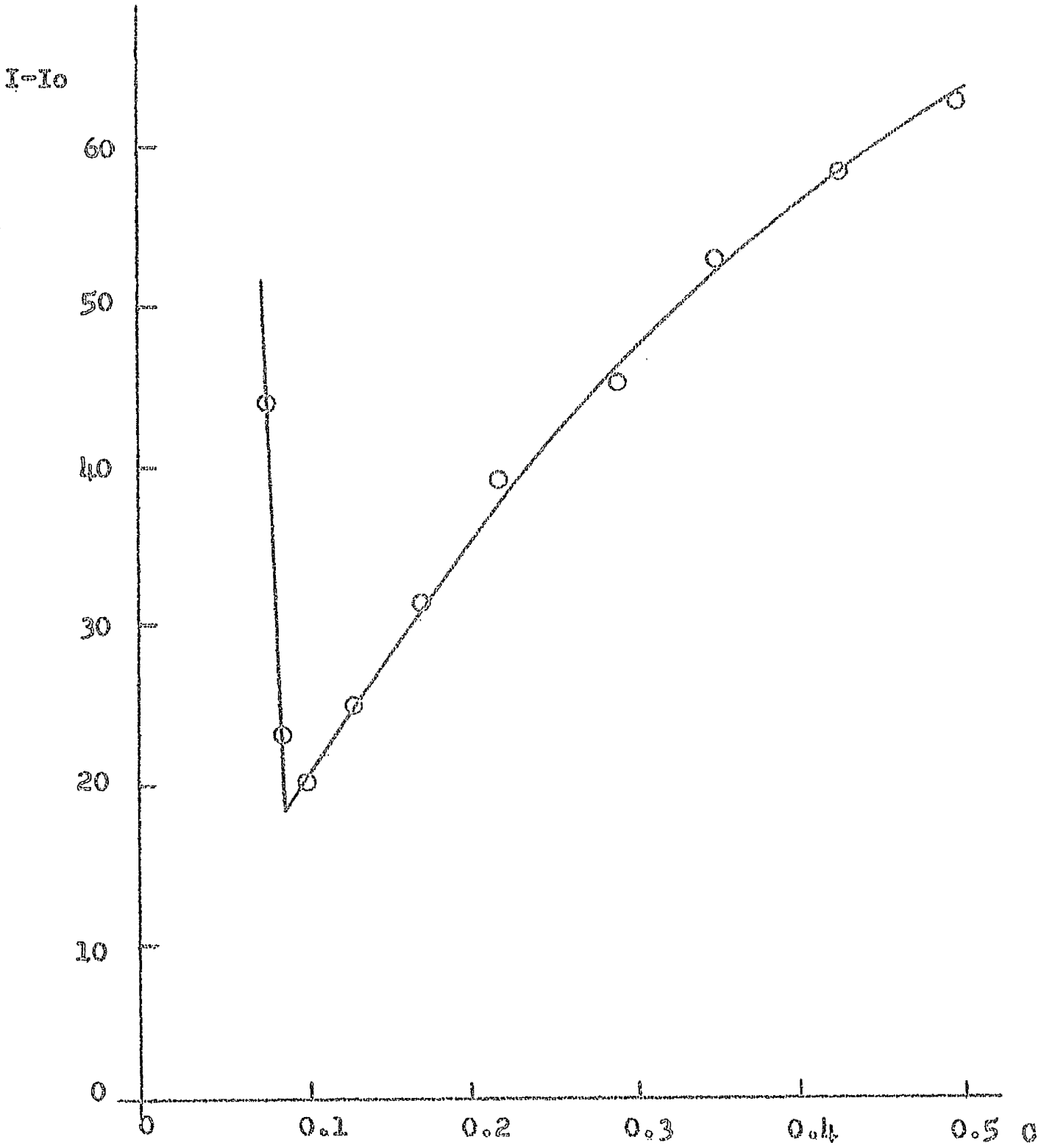
GRAPH 38B

H.T.A.B. + OCTANOL 0.099 gms./100 ml. 1% at 25°C



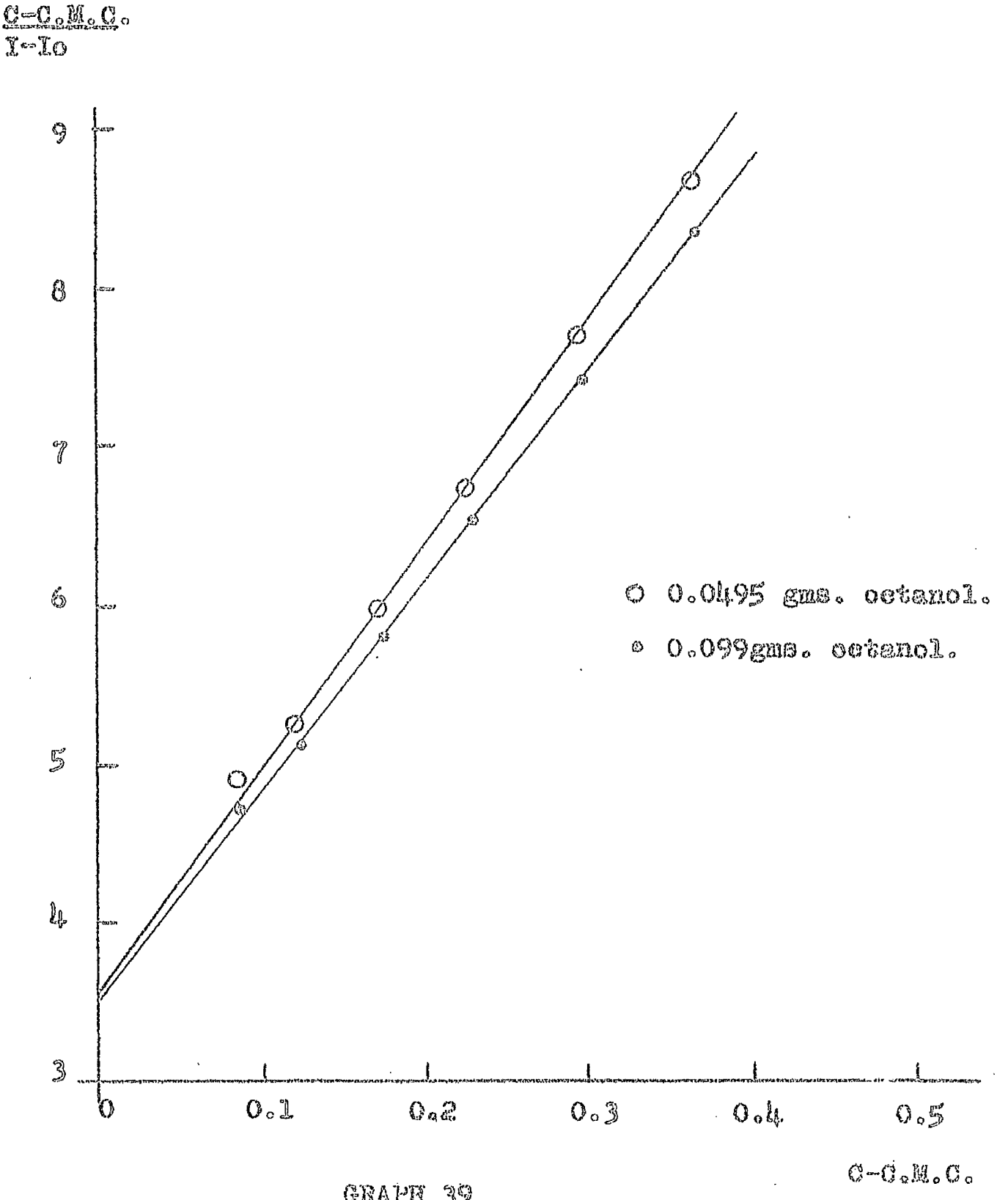
GRAPH 38C

H.T.A.B. WITH OCTANOL 0.1484 gms./100 ml. 1% at 25°C



GRAPH 38D

H.T.A.B. + OCTANOL AT 35°C



GRAPH 39

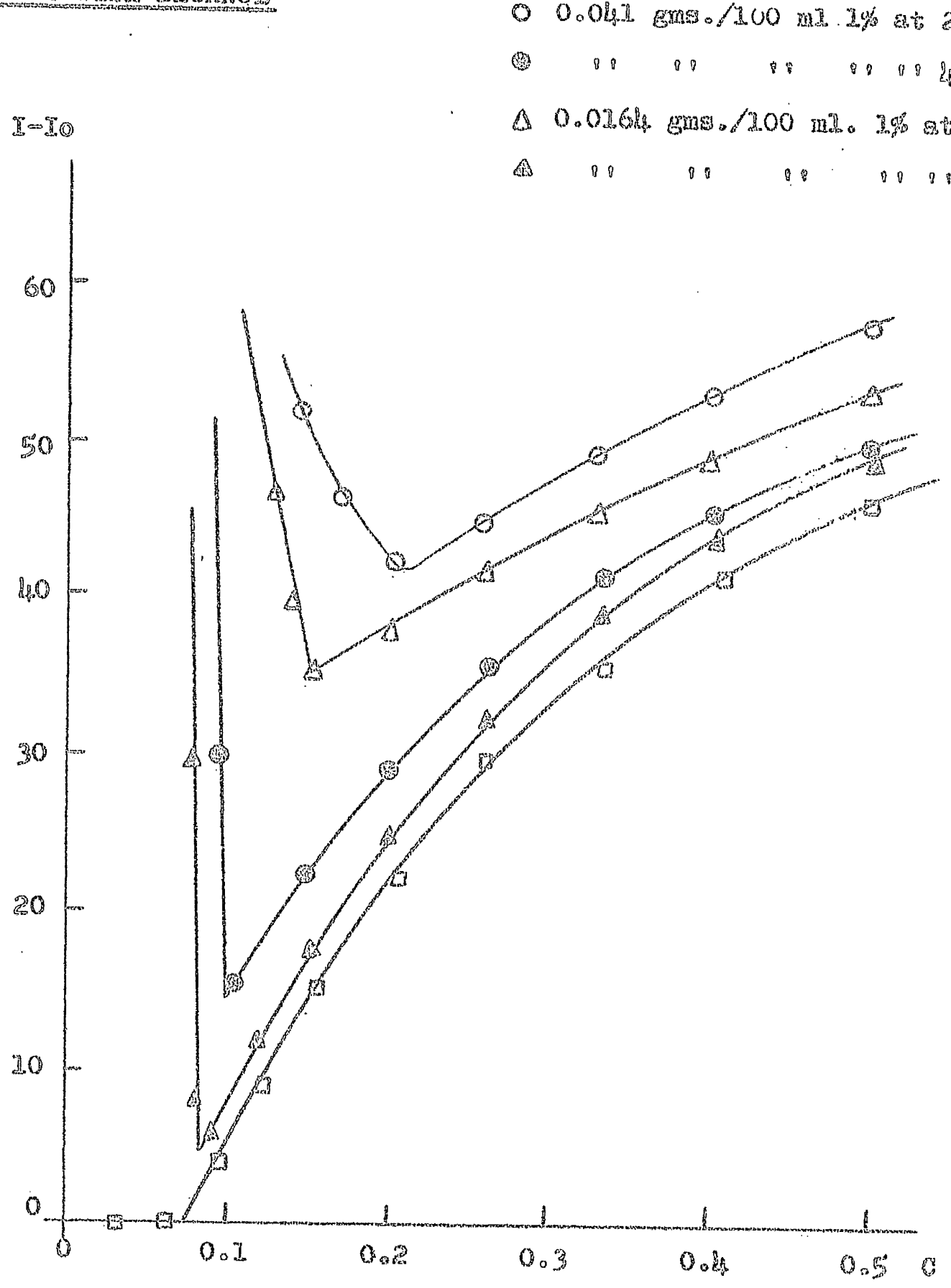
Solubilizate	Amt. Alcohol gms./100ml. 1%	Monomer Conc. gm./100ml. $\times 10^2$	Lim. $\frac{C-Co}{I-Io}$ $\times 10^3$	$\frac{dn}{dc}$	Apperent Micellar Weight.	No. of Soap Molecules /Micelle	No. of alcohol molecules /micelle.
OCTANOL	0	7.8	3.7	0.143	26,100	72	0
mol. wt. 130.2	0.0495	6.5	3.55	0.145	26,500	69	10
n^D =1.4292	0.099	6.0	3.46	0.145	27,000	67	20
Density 0.8246							

TABLE 12.

there appears to be a reduction in the number of soap molecules per micelle, the mixed micellar weight remaining almost constant by replacement of some of the soap molecules by solubilized alcohol. In all the cases considered previously, except for small additions of benzene, the reconstitution due to solubilized hydrocarbon led to an increase in the association number. The partial insolubility of the long chain alcohols in the micelles is no doubt due to their proximity to the aqueous component, being located at the micellar surface. They are not shielded to the same extent as solubilized material is in the micelle interior and, being loosely bound, there exists the possibility that they can enter the aqueous layer and coalesce with other alcohol molecules. This could explain the observed increase in scatter at lower temperatures.

With decanol (graph 40) the scatter due to unsolubilized material is even more acute. Even with only 0.0164 grams of decanol at 45°C the superficial increase in scatter at low soap concentrations is evidenced. The break point is

H.T.A.B. WITH DECANOL



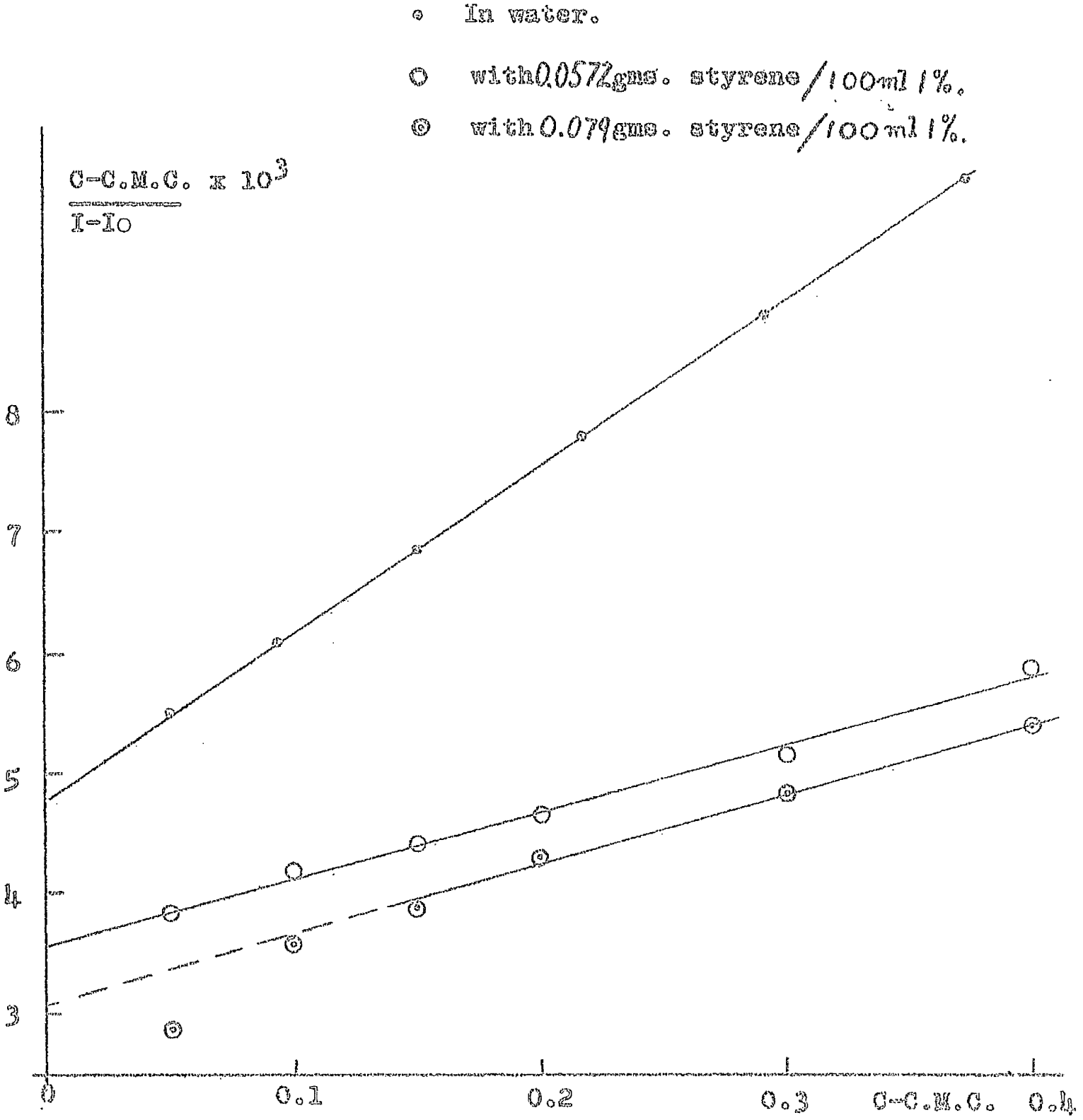
GRAPH 40

shifted to regions of higher soap concentrations than the original C.M.C. with increasing amounts of decanol and with decreasing temperatures. Thus instead of stabilizing the micelles by solubilization small additions of decanol enforce their dis ociation making an analysis of micellar weights from light scattering data impossible.

Styrene Solubilized in S.U.S.:-

The few experiments carried out with styrene as additive in S.U.S. solutions showed similar trends to the solubilization of other hydrocarbons in H.T.A.B., except that there was very little abrupt increase in scatter at low concentrations of soap. The styrene appears to be capable of stabilizing the micelle to dilute regions well below the original C.M.C.: and for the small amounts of styrene added $\frac{C-C.M.C.}{I-Io}$ versus C-C.M.C. curves were readily constructed (graph 41). In an analogous manner to previous investigations the mixed micellar weight increased to 34,250 from 30,800 on the addition of 0.079 grams of styrene. This is accounted for both by incorporation

SODIUM UNDECENYL SULPHATE + STYRENE



GRAPH 41.

of the additive in the micelle and a rearrangement of the number of soap molecules per micelle leading to a higher association number.

CONCLUSIONS:-

The difficulties associated with the interpretation of the results from light scattering by soap solutions, as discussed in part I of this thesis, undoubtably apply in the case of solubilized solutions. The results tabulated in this section on solubilization are thus subject to some uncertainty which is difficult to eliminate, but qualitatively at least the following information concerning the change in the properties of micelles accompanying solubilization has been gathered:-

(1) There is a vast increase in the light scattered by all the solubilized systems below the C.M.C.. This is attributed to an aggregation of solubilizate molecules, after the commencement of dissociation of the micelles, to form droplets which scatter a large amount of light.

(2) The C.M.C., as determined by the point where the vast increase in scatter is recorded, decreases monotonically with an increase in the concentration of solubilizate. This is best understood by considering the incorporation of a hydrocarbo

in the interior of the micelle as effectively increasing the chain length of the H.T.A.B. molecules.

[It is a well established fact that the C.M.C. decreases as one progresses along a homologous series of soaps.]

This illustrates how closely the configuration of the paraffin chains within a micelle must resemble that of a liquid.

(3) Good linearity of the $\frac{C-C.M.C.}{I-Io}$ v's C-C.M.C. curves at soap concentrations from 0.2 to 1% suggests that the micelles containing solubilizate may be of approximately fixed composition in this region.

(4) The increase in micellar weight on solubilization of a hydrocarbon is accounted for not only by the incorporation of additive in the micelle interior, but also by an increase in the number of detergent molecules per micelle. Thus solubilization proceeds with a reorganisation of the micelle. Presumably the enlargement of the micelle on receiving solubilizate disturb the balance of forces at its surface. This can only be

conserved by the inclusion of more detergent molecules per micelle.

(5) With polar additives the association number appears to decrease on solubilization. This can be accounted for by simple replacement of some of the detergent molecules by the alcohol.

(6) With octane and cyclohexane as addititives the change in micellar weight accompanying solubilization can be expressed in terms of a linear plot of micellar weight versus the molar ratio of additive to soap. This empirical relationship seems to be restricted to these two hydrocarbons.

(7) Small additions of solubilizate (up to 7 molecules per micelle for cyclohexane) make little or no impression on the aggregation number of H.T.A.B., whereas subsequent addition causes a significant change. This suggests that there is a certain space available for solubilization within a micelle before its aggregation number is altered by the solubilizate.

(8) No definite conclusions can be drawn from the results with

benzene as the solubilizate. The dramatic reduction in the association number of the micelles on small additions of benzene followed by an increase after a certain amount has been added seems highly improbable. The error probably lies in the correction factor used for the solvent, since aqueous benzene must be considered instead of pure water. The relative amounts of benzene used for this purpose were calculated from the distribution measurements. Since this attempt to calculate the partition coefficient between benzene in the water and solubilized benzene was based on a rather naive model it is possible that the calculations involve considerable error.

(9) All the additives, except for benzene, seem to be solubilized to approximately the same extent. Past reports (90,94) that an increase in the polarity of the solubilizate increased the extent of solubilization are incorrect if the solubilization limit is detected instrumentally. It is apparent from the light scattering measurements that octanol and decanol are undissolved below the visible saturation limit.

It is impossible to separate the light scattered by the micelles from that by the undissolved alcohol, except by raising the temperature of the solutions. This renders the unsolubilized alcohol water soluble.

The fact that octanol and decanol are partly unsolubilized below the visible saturation limit is probably due to their proximity to the aqueous layer, being located at the micellar surface. Being loosely bound the situation exists whereby the alcohol may leave the micelle and aggregate to form emulsion droplets.

The relatively high solubility of benzene (0.185 gms./ 100 ml. 1% H.T.A.B. C.F. 0.165gms./100 ml. 1% H.T.A.B. for octane) can be attributed to its water solubility (0.171gms./100 ml.), its low molar volume and the possibility of a dual locus for solubilization. As a hydrocarbon it can be located in the micelle interior and also, due to its polarisability, orientated at the micellar surface.

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